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OF THE
AMERICAN LEATHER CHEMISTS ASSOCIATION

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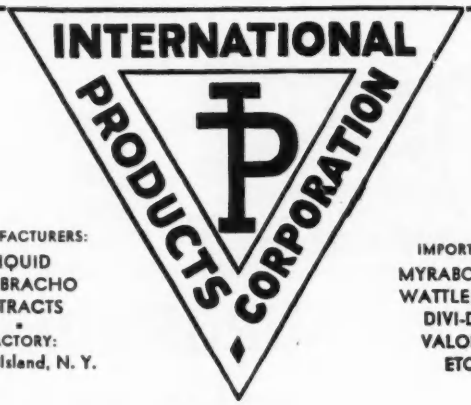

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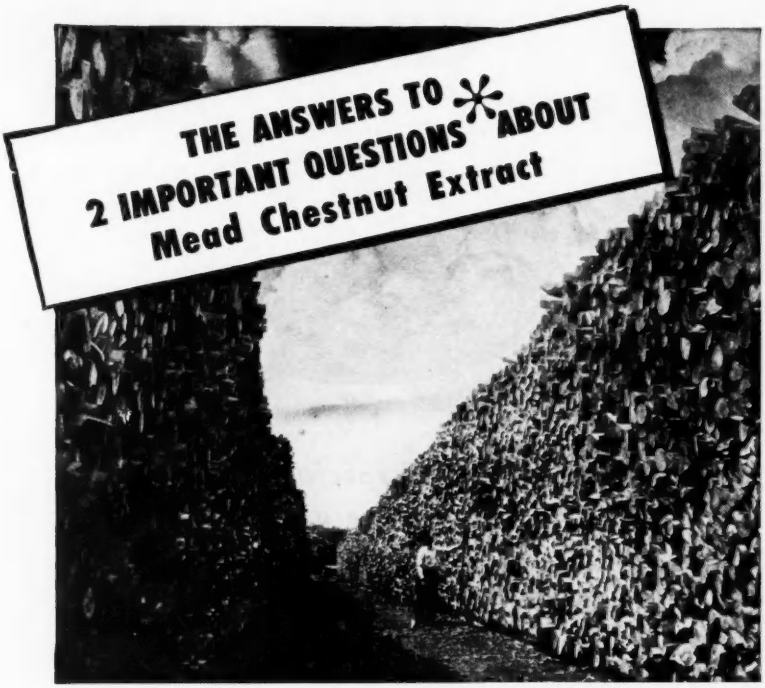

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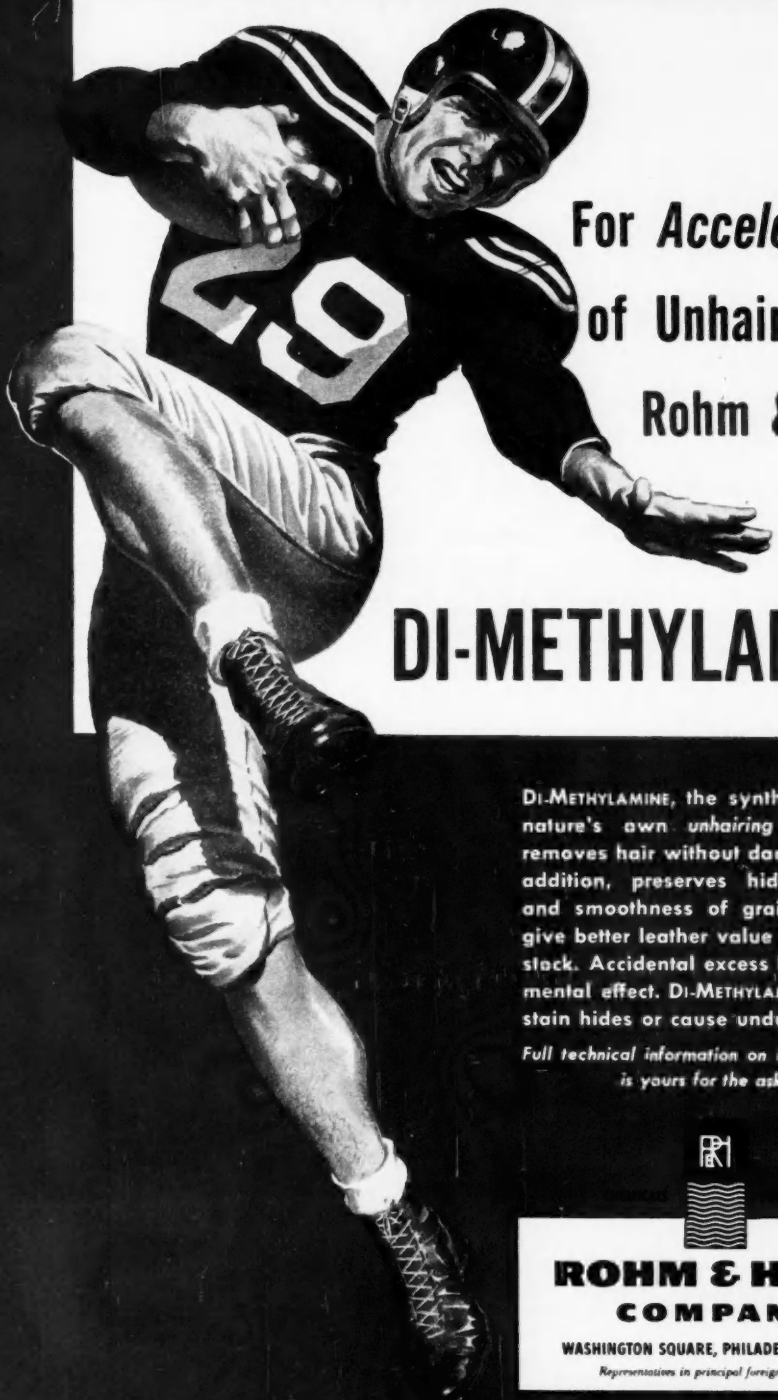

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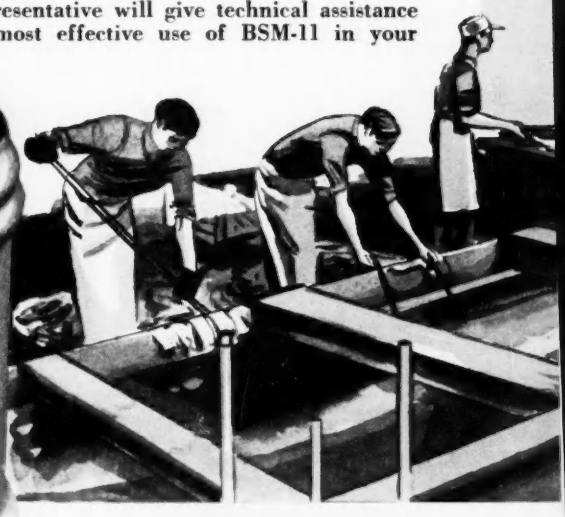

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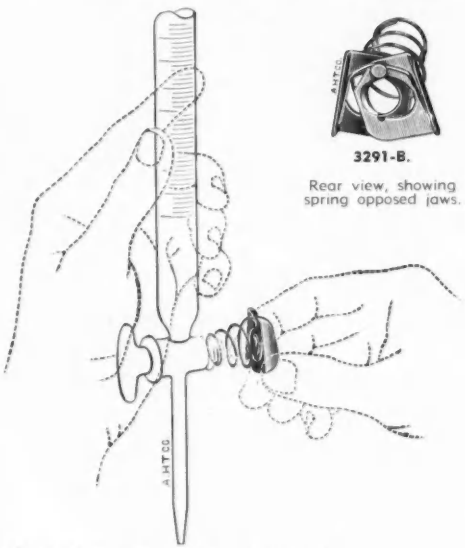

3291-B. Method of attachment or removal.

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Rear view, showing spring opposed jaws.

3291-B. In position.

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COUNCIL MEETING MINUTES

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

NOVEMBER 13, 1952
WASHINGTON, D. C.

The meeting was held at the Hotel Statler at 10:00 A. M.

Present were President Turley, Council Members Collins, Hobbs, Morrison, Ross, and Windus; also Messrs. Williams, Teas, Kirk, Meo, Hague, Maeser, and O'Flaherty.

The minutes of the June 1st and 3rd meetings were given final approval.

Dean Williams reported a request that on abstracts in the Journal the address or business connection of the author be included. Council agreed that it was not necessary.

President-Elect Flinn was unable to attend, but Dr. O'Flaherty had spent the previous day at Chillicothe with Dr. Flinn and reported for him.

Dr. Flinn wanted to know whether the International Commissions were a part of his responsibility. He was advised that the responsibility for the International Commissions should be in the hands of our delegates, preferably our member of the International Executive Commission. At the present time, Dr. Turley is a member of this Executive Commission.

A list of the various committees were reviewed and the personnel checked. There were several in question. The Secretary is to complete this record and have it published in the Journal.

Dr. Flinn, the Editor, and the Secretary were appointed as a committee to do final editing of methods before publication, to conform to the By-Laws.

No reports were available on the French Hide Powder Committee or the Engineering Committee. Council voted to drop these two committees.

Dr. Flinn asked for instructions on the size of the page and numbering of the methods booklet. Council approved the present size because it is the same as the Journal and is more economical than any other size.

The Editing Committee is to work out a numbering system along the present line of alphabet and numbers with the initial being indicative of the section.

No report from the Vegetable Leather Committee.

Council requested the Secretary to advise Mr. Kay that he should prepare for publication the presently acceptable portion of methods on Tannin Analysis and to delete the sampling procedure which should be placed in a subsequent chapter on Sampling and Testing.

Mr. Maeser was present and reported he would have completed twenty-two methods by December 20th, and would send them to be published.

It was agreed that all physical tests would be presented as provisional as so many changes have been made which were more than in detail.

Mr. Maeser reported the comment of Dr. Lollar on the test result interpretation and Council feels that such information would be valuable and

should be included in the chapter on Sampling and Reports.

The status on the Mineral Tannage Method is as published and should be brought up for vote at the next annual meeting.

The Mechanical Leather Committee is being organized by Mr. Berens, who is to send a list of members to the Secretary and will also present a program for his committee later.

Dr. Seligsberger has reported to Dr. Flinn that his Committee on Mineral Tannage will proceed with committee work on zirconium and on sulfur analysis.

Council requested that all methods be published as soon as approved by the Editing Committee with copies sent to all active members and that sections be sold at cost plus 25 per cent to others.

Council, in considering the report of the Preparatory and Post Tanning Committee, requests that the nitrogen analysis as suggested by this committee as well as the fat extraction method be adopted as provisional methods.

There should be two methods on extraction, and they should be titled Petroleum Ether Extractable Material and Chloroform Extractable Material.

Council requested the Secretary to write to Dr. Flinn and ask him to contact each technical committee chairman to get a report on their work to date and then to make a resume of same for publication in the Journal.

The matter of testing all lots of French Hide Powder was considered and Council agreed that if our commission were to test one lot a year that would be sufficient, as it is not used officially in the U. S. except in case of International Involvement. Mr. Clarke is to be so advised by Dr. Turley, who is a delegate of the International Union. Mr. Clarke will in turn advise the chairman and ask which lot they want tested.

The matter of a contract between Mr. Marshall and the A.L.C.A. was considered and upon motion by Mr. Morrison, seconded by Dr. Windus, it was unanimously agreed that the matter should revert to its original status and no contract considered necessary.

The Secretary is to so advise Mr. Marshall, also expressing the appreciation of the A.L.C.A. for the continued production of standard hide powder. Dr. Turley is to advise our attorney of such.

The transcript of the Symposium, conducted by the New England Production Club was submitted by Editor Williams. After due consideration it was moved by Dr. Windus, seconded by Mr. Collins, that a separate supplement of the Journal be printed to record this report and that a copy be given to each member of the New England Production Club. This was unanimously approved by Council.

Mr. Morrison, Chairman of the Committee appointed to cooperate with Leather Industry of America, reviewed his correspondence with Messrs. Van Pelt and Glass and reported that he was advised that this Committee would be called upon soon by Mr. Glass.

A brief financial statement with estimated expenditures was presented

and it indicated that the operations of the Association would result in no deficit for 1952.

The following candidates were elected to active membership:

ROMERO PESSOA DE SOUZA
RICHARD E. NEVETT
HENRI V. KRAKOWSKI
ANDREW JOHN GARD
RICHARD CURTIS CAMP

The following membership was transferred from associate to active membership:

C. ALLAN LAUDER

Messrs. Kirk, Meo, and Hague reported on their plans for the 50th Year Meeting and Council approved their plans.

They reported that Dr. Kirk, serving as Chairman, had delegated entertainment and hotel arrangements to Mr. Meo and publicity to Mr. Hague.

The Publicity Committee will serve under Mr. Hague and consists of Mr. Drew for New England, Mr. Miller for the Middle West, Mr. Brydon for Canada and Dr. O'Flaherty. Mrs. A. Boss is to be in charge of the women's activities.

Suggestions of persons to serve on the Award Committee were made to President Turley, who will make the appointments.

Consideration was given by Council to the establishment of a Jubilee Fellowship for some younger member to travel to foreign centers of tanning technology. Council was not in favor, so the matter was dropped.

Council approved the increase of the Editor's clerical expenses to $50.00 a month.

In considering the meeting place for 1954, Lake George and Spring Lake were suggested, and Dr. Kirk is to inquire regarding same.

Council agreed to hold its next meeting at Philadelphia, Thursday, February 12, possibly at the Sylvania Hotel.

Respectfully submitted,

FRED O'FLAHERTY.

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Physical Testing ..... M. Maeser

International Tannin Analysis Commission
American Representative ..... A. N. Kay

Committee Recently Discharged

New Analytical Techniques
French Chrome Hide Powder
Engineering

Studies Concerned with the Structure of Collagen*

Part III. The Stress-Strain Behavior of Thermally Contracted Formaldehyde Tanned Collagen.

By Norman M. Wiederhorn, Gerald V. Reardon, and Alice R. Browne

United Shoe Machinery Corporation
Research Division
Beverly, Massachusetts

Introduction

In a previous communication, the stress-strain behavior of thermally contracted (denatured) collagen was reported [1]. Here it was demonstrated that when swollen in appropriate media, the denatured protein obeys the kinetic theory of rubber elasticity, provided it is not too highly extended. Furthermore, assuming collagen to be a network polymer consisting of long chains tied together at intervals along their length, the average molecular weight of the chain between points of primary valence crosslinking was shown to be of the order of 55,000. This figure may be compared with a molecular weight calculated from X-ray data (60,600) [1], and the molecular weight of procollagen (soluble collagen) obtained by ultracentrifuge measurements (70,000) [2]. In view of the errors involved in the stress-strain (ca. 10%) and

*Presented at the Forthy-Eighth Annual Meeting, Swampscott, Mass., June 2, 1952.

ultracentrifuge measurements (probably 10 to 15%), these molecular weights are in fair agreement and establishes the former as a perfectly valid method for investigating the molecular weights of collagen.

The objective of the work to be discussed now was to investigate the effect of formaldehyde tannage upon the stress-strain behavior of denatured collagen fibers. The treatment of the collagen of hide with formaldehyde is one of the more important industrial tannages. It has been studied extensively, but because of the complexity of the reactions many of the details of the system are unknown. One of the more debatable aspects, which as yet has not been answered, is the extent to which formaldehyde crosslinks the collagen molecule. Fraenkel-Conrat has demonstrated which amino acid residues may take part in a crosslinking reaction [3]. However, quantitative data with the native protein is lacking.

From the stress-strain behavior of a thermally contracted sample, a molecular weight between points of crosslinking may be determined. From this quantity it is possible to calculate the number of crosslinks per unit volume or mass. The theoretical basis for the interpretation of such measurements has been presented elsewhere [1, 4]. Consequently, only a review of the highlights of the theory will be given here.

An ideal crosslinked rubber may be considered to be a network of flexible chains tied together at various points along their length by linkages whose stability approximates that of the bonds which comprise the chain. (See Figure 1). The junction points of such a system normally are referred to as points of crosslinking. Furthermore, there must be no attractive or repulsive forces between different chains or various portions of the same chain. The stress-strain behavior of such a material is uniquely determined by just three

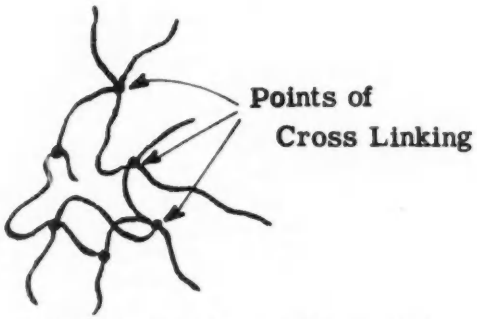


FIGURE 1.—The Idealized Rubber Net Work.

parameters of the sample, namely: its density, the length of the chain between points of crosslinks, and the fraction of the total volume of the sample which is occupied by the network. (The sample may be swollen in a solvent. In

such an instance the volume consists of two components, the rubber network and the swelling medium.) The mathematical relation correlating the retractive force with the elongation of the sample is simply

$$f = \frac{v_2^{1/3}}{M_c} RT\rho(\alpha - 1/\alpha^2) \quad \ldots\ldots 1$$

where

f is the retractive force per unit cross-section.

α is the relative elongation of the sample, i. e., the ratio of the stretched length to the intial length.

ρ is the density of the unswollen rubber.

T is the temperature in degrees absolute.

R is the gas constant (8.478×10^4, if the force is given in gm/cm^2 and the density in gm/cm^3; or 1.736×10^5, if the force is in pounds per square foot and the density in gm/cm^3).

M_c is the average molecular weight of the chains between crosslinks.

and v_2 is the volume fraction of the rubber constituent in the sample.

The utilization of this equation to determine molecular weights between crosslinks is straightforward. If f, the retractive force, is plotted against $v_2^{1/3} RT\rho(\alpha - 1/\alpha^2)$, a straight line going through the origin should be obtained. The slope of this line is simply 1/Mc.

It must be emphasized that Equation 1 is only applicable if the sample is an ideal rubber, i.e., if it is a simple network composed of flexible chains and there are no attractive or repulsive forces between the various chains or portions of the same chain. It has been demonstrated that thermally contracted collagen when swollen in water, formamide, or a one molal solution of LiCl in 1:1 water-ethanol fulfills these criteria.

Measurements of this type are sentitive to relatively small changes in the number of crosslinks and also are one of the few methods for obtaining a quantitative estimate of their concentration. Swelling measurements have been used to determine Mc for a number of simpler polymeric materials, but their applicability to formaldehyde tanned collagen is questionable. This is a consequence of the fact that the extent to which a material will swell in a particular swelling medium is a function of two factors, the concentration of crosslinks and the interactions between the polymer and the medium. When collagen is reacted with formaldehyde, both of these quantities change; and it is not possible to unequivocally partition the decrease in swelling between the two variables. The change in the polymer-solvent interaction is due to the fact that formaldehyde undergoes various reactions other than crosslinking with the protein. The base material is thus altered and, consequently, its interactions with the swelling medium could not be expected to remain unchanged.

Experimental:

Preparation of Samples:

Kangaroo tail tendons were employed as the source of collagen as this is a form of collagen which is amenable to the type measurements which were made. In addition, it is a relatively pure form of the protein. Before tannage, the collagen was purified by extraction with a 10 per cent sodium chloride solution to remove globular proteins. This was followed by an extraction with diethyl ether to remove fats. The tendons obtained in this manner were tanned at room temperature for ca. 65 hours in 0.1 M phosphate buffers at pH's ranging from 3 to 9. The concentration of formaldehyde in the tanning bath varied from 0.3 per cent to 10 per cent. After removal from the tanning solution, they were washed for eight hours with cold running water to remove the salts and unreacted formaldehyde. They were then denatured (contracted) by placing them in boiling water for ca. two to three minutes, and, finally, air dried and stored in this condition until they were used.

Prior to use the samples were conditioned by soaking in water at room temperature overnight and then for four hours at the temperature at which the stress-strain measurement was to be run.

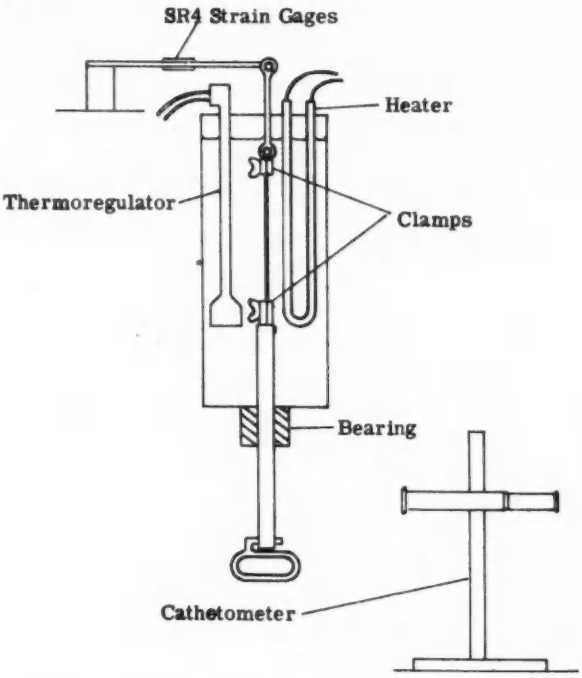


FIGURE 2.—Diagram of equipment employed for Stress-Strain Measurements.

Stress-Strain Measurements and Volume Fraction Leterminations:

The procedure employed for these measurements was described in detail previously [1]. Basically it consisted of mounting the sample between two clamps which were immersed in water. (Figure II). The upper clamp was attached to a cantilever beam on which was mounted a calibrated SR 4 strain gage. The lower clamp was mounted on a rigid rod which chould be moved vertically, thus extending the sample. After carrying the sample through a cycle of elongation and retraction, it was cut from the clamps, blotted with filter paper, and its mass, length, and density determined. From these quantities its cross-section was calculated. The sample was then dried with acetone, followed by desiccation over P_2O_5 and, finally, placed in a vacuum oven at 70°C. From the dry weight thus obtained, and the wet weight obtained previously, the volume fraction of the protein in the sample was calculated.

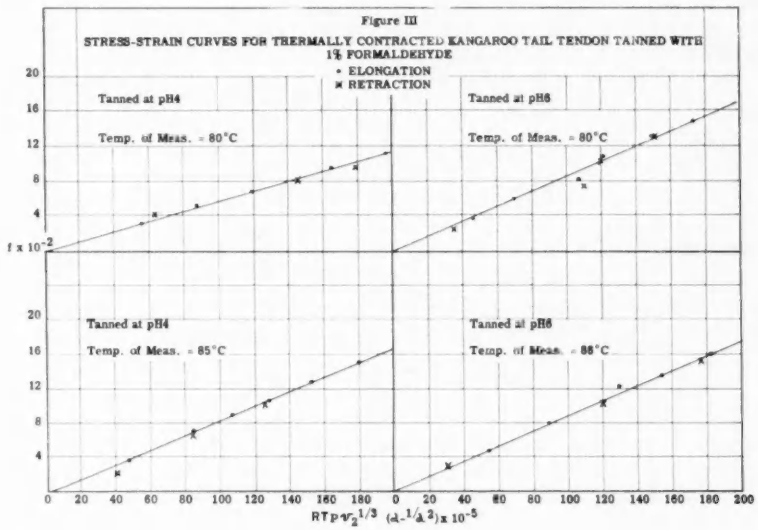


Figure III
STRESS-STRAIN CURVES FOR THERMALLY CONTRACTED KANGAROO TAIL TENDON TANNED WITH 1% FORMALDEHYDE
• ELONGATION
× RETRACTION
Tanned at pH4
Temp. of Meas. = 80°C
Tanned at pH6
Temp. of Meas. = 80°C
Tanned at pH4
Temp. of Meas. = 85°C
Tanned at pH6
Temp. of Meas. = 85°C
f x 10^-2
RTρv2^1/3 (α-1/α2)x 10^-5

Results:

The stress-strain measurements were all made at temperatures exceeding 65°C. Below this temperature the samples do not obey rubber elasticity theory. The data for tendons which were tanned with 0.30, 1.0, 3.0, and 10 per cent formaldehyde are given in Table I. The values for Mc, the molecular weight between cross-links, were obtained from the slopes of the initially linear portion of plots of f vs. $RT\rho\, v_2^{1/3}(\alpha - 1/\alpha^2)$. (See Figure III). From the molecular weight between crosslinks, the number of cross-links introduced by formaldehyde into the collagen chain may be calculated. Using a figure

TABLE I

% Form.		pH of Tannage 2	3	4	4.6	5	6	7	8	9	10
	Mc		Samples Decomposed After Conditioning	>40,000	38,000± 7,000	16,000± 1,000	14,000± 2,000	19,000± 1,000	20,000± 4,000	13,000± 2,000	17,000±
	No. of Meas.			4	2	3	4	4	4	2	5
0.3%	F**			< .001	c.a. .001	.0023	.0054	.0081	.011	.014	.017
	v			< 0.4	0.45	2.5	2.9	1.9	1.8	3.3	2.3
	f			>70.22	c.a. 0.25	0.70	0.32	0.13	0.09	0.13	0.07
	Mc	Samples Decomposed After Conditioning	29,000±	15,300±		16,600± 1,000	13,300± 2,000	12,500± 1,600	15,000± 1,000	13,900± 2,400	16,000± 2,500
1%	No. of Meas.		2	3		3	3	3	2	3	3
	F**		c.a. .001	.0023		.0057	.0089	.012	.013	.017	.023
	v		0.9	2.6		2.3	3.2	3.5	2.7	3.0	2.5
	f		c.a. 0.49	0.61		0.21	0.19	0.16	0.11	0.10	0.06
	Mc							15,900± 500			
3%	No. of Meas.							3			
	F**							0.016			
	v							2.5			
	f							0.09			
	Mc							11,400± * 1,200			
10%	No. of Meas.							6			
	F***							0.019			
	v							3.9			
	f							0.11			

*Three samples conditioned at 80°C. for three hours and the other three for 24 hours.
**Extrapolated from the data of Highberger and Retzsch.
***Extrapolated from the data of Highberger and Salcedo.

of 92.6 for the average residue weight of an amino acid in collagen, the number of residues between points of crosslinking is:

$$R_c = M_c/(92.6 + 92.6F) = M_c/92.6(1 + F) \quad \ldots\ldots 2$$

where

R_c is the number of amino acid residues between crosslinks.

M_c is the molecular weight between crosslinks.

and F is the grams of bound formaldehyde per gram of collagen. The necessity for including the second term in the denominator of Equation 2 arises from the fact that once formaldehyde is combined with the collagen, the average residue weight is increased by this quantity. This term is normally small, and is only approximately 4.5 per cent of the first term even under those conditions where the greatest formaldehyde binding was obtained (pH 10 with 1.0 per cent formaldehyde in the tanning bath).

With collagen which has not been tanned

$$R_{co} = \frac{M_{co}}{92.6} \quad \ldots\ldots 3$$

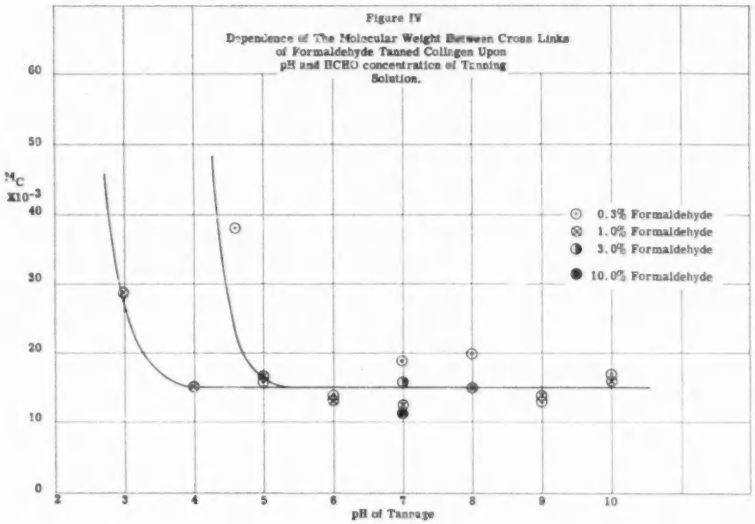
where the second subscript refers to untanned material. The number of new crosslinks which have been introduced per unit of M_{co} due to tannage, is thus

$$v = \frac{R_{co}}{R_c} - 1 = \frac{M_{co}}{M_c}(1 + F) - 1 \quad \ldots\ldots 4$$

Previously, Mco has been determined by the same method described here to be 55,000. Using this quantity (although x-ray data indicates that 60,000 may be a better figure) and the data of Highberger and Retzsch for the amount of formaldehyde fixed per gram of collagen, the values of "v" listed in Table I were calculated. Also included are the values for F taken from the data of Highberger and Retzsch and Highberger and Salcedo[5, 6] and the fraction of the reacted formaldehyde which is actually involved in forming crosslinks. This quantity $\overline{f}$ was calculated from the relation:

$$\overline{f} = \frac{30v}{55{,}000F} = \frac{5.5 \times 15}{F}\left(\frac{M_{co}}{M_c}(1 + F) - 1\right) \quad \ldots\ldots 5$$

In Figure IV the molecular weight between crosslinks is plotted against the pH of tannage. As can be seen, there is considerable scatter of the experimental points. However at pH 5 and above, a comparatively constant value of M_c (c. a. 15,000) was obtained, independent of pH of tannage or concentration of formaldehyde in the tanning solution. Below approximately pH 5, the molecular weight between crosslinks increases markedly and is dependent upon the formaldehyde concentration. Significantly, the molecular weight between crosslinks of untreated tendon is of the order of 55,000, whereas at the lower pH's values exceeding this were obtained. This presumably is a consequence of an acid catalyzed hydrolysis of the sample. This has been demonstrated to occur at an appreciable rate[7] with tendons



stored at room temperature in media below pH 4. The samples tanned with 10 per cent formaldehyde were tested after they had been conditioned at 80°C. for eight hours. When the normal conditioning cycle was employed, extremely low molecular weights were obtained. On the other hand, when the samples were maintained at 80°C. for twenty-four hours before testing, the molecular weight did not change within experimental error. The results are given in Table II.

TABLE II

Dependence of M Upon Time of Conditioning at 80°C. for Tendons Tanned with 10 per cent Formaldehyde at pH7—Temperature of Test 80°C.

Time	Mc	Number of Samples
4 hours	6,900 ± 600	4
8 hours	11,300 ± 1,100	3
24 hours	11,400 ± 900	3

Discussion:

It is generally accepted that at low concentrations of formaldehyde (below ca. 3%) and at pH's below 7 to 8 the only side groups in collagen which react directly with formaldehyde are the amino groups of lysine and hydroxylysine[3, 5, 6]. The product of this reaction presumably may then combine with the primary acid amide groups of asparagine and glutamine, or the guanidyl group of arginine. The crosslinks formed in this manner presumably consist of methylene bridges, i. e.

$$R\text{-}NH_2 + CH_2O \longleftrightarrow R\text{-}NH\text{-}CH_2OH \quad \text{I}$$

$$\begin{array}{l} H \\ R\text{-}N\text{-}CH_2OH \end{array} + H_2N\text{-}\underset{H}{\overset{H}{C}}\text{-}R^{1} \longleftrightarrow R\text{-}\underset{H}{N}\text{-}CH_2\text{-}\underset{H}{N}\text{-}\overset{H}{C}\text{-}R^{1} \quad \text{IIa}$$

$$+ H_2N\text{-}\underset{NH}{\overset{H}{C}}\text{-}N\text{-}R^{11} \longleftrightarrow R\text{-}\underset{H}{N}\text{-}CH_2\text{-}\underset{H}{N}\text{-}\overset{H}{C}\text{-}R^{11} \quad \text{IIb}$$

$$\begin{array}{l} \\ \| \\ NH \end{array} \qquad\qquad \begin{array}{l} \\ \| \\ NH \end{array}$$

At higher pH's where the uptake of formaldehyde is markedly increased, it has been suggested that in addition to the amino groups the guanidyl residues may react directly [5, 8, 9]. However, the interpretation of results in this pH range is complicated because of side reactions of formaldehyde, i. e., polymerization and the Cannizaro reaction. On the basis of the results presented in Table I and Figure 2 it is apparent that above pH 5, the extent of crosslinking is essentially independent of the quantity of formaldehyde reacted and the pH. This is in complete agreement with the statements just made. The dependence upon pH is readily explained by assuming that reactions I and II are the only reactions which will introduce crosslinks.

The combination of formaldehyde with the amino groups in the collagen side chain occurs throughout the pH range investigated, but below pH 7 to 8 these groups are only partially reacted. Now, the maximum number of crosslinks which formaldehyde introduces per fundamental 55,000 unit of molecular weight is approximately three. (This figure is obtained by averaging the values for "v" in Table I; i. e., 2.7 ± 0.6 s.d.). Consequently, complete crosslinking could not be hoped for unless at least 3 mols of formaldehyde have reacted with 55,000 gms. of collagen. This corresponds to 0.0016 grams of formaldehyde per gram of collagen. With a 0.3 per cent formaldehyde solution, this minimal quantity will be bound at a pH between 4.6 and 5. With a 1 per cent formaldehyde solution, the pH must be 3 to 4. However, it is precisely in these pH ranges that cross-linking becomes complete, i. e., approximately three crosslinks are introduced per 55,000 molecular weight unit (Table I). Thus the dependence of "v" and the molecular weight between crosslinks upon the pH of tannage and the concentration of formaldehyde in the tanning bath, is apparent. When the pH and formaldehyde concentration are such that greater than approximately 0.0016 grams of formaldehyde are bound per gram of collagen, maximum crosslinking will occur. At lower pH's, less than maximum crosslinking takes place and the molecular weight between crosslinks will be greater than the minimal value of approximately twelve to eighteen thousand. As a matter of fact, at sufficiently low pH values hydrolysis may occur. In such cases the molecular weight between crosslinks may exceed the value of 55,000 for the untreated material and may lead to extensive decomposition of the sample.

However, not all the amino groups partake in the crosslinking reaction. This may be seen from Bowes and Kenton analysis of the amino acid com-

position of collagen, for there are between 21 and 24 amino residues in the fundamental unit of 55,000. In addition, the non-quantitative conversion of amino groups to crosslinks is not due to a deficiency of acid amide or guanidyl residues for reactions II a and II b, as there are 27 and 30 of these groups respectively in the unit. Another explanation must be sought.

For either reaction II a or II b to occur, it is necessary that the methylol addition product of reaction I be relatively close to an acid amide or guanidyl group. Since the chain in a collagen fibre is restricted in its motion, being in a crystalline lattice, an amino methylol derivative can not approach an acid amide or guanidyl group simply because of random Brownian motion. Crosslinks can only be formed from the reaction of those groups which are close as a consequence of the structure of the collagen molecule. Therefore, the fact that but a fraction of the amino groups take part in a crosslinking reaction is not unexpected. Apparently, only about three amino residues or one in seven or eight, is located geometrically favorably.

Another point of interest revolves about the equilibria of reactions I and II. At pH's below about 8, the only side groups which react directly with formaldehyde are the amino groups of lysine and hydroxy lysine. Thus at these pH's the fraction of the bound formaldehyde which is utilized in forming crosslinks $\overline{f}$ is also the fraction of the amino groups which has undergone one of the crosslinking reactions (II a or II b). Now the fraction of the amino groups which can undergo the crosslinking reaction is only one in seven or eight, or ca. 0.12 to 0.15. However, at pH's below 8, values of $\overline{f}$ are found which greatly exceed this figure indicating that at these lower pH's there is a marked tendency for the formaldehyde to react preferentially with those amino groups which are sterically capable of undergoing reactions II a or II b to form crosslinks. This, of course, is also evidenced by the fact that crosslinking is essentially complete when only the minimal or slightly more than the minimal quantity of formaldehyde for complete crosslinking has reacted. From these observations it is possible to conclude that the equilibria for eactions II are far to the right, and that reaction I is reversible. If these conditions are fulfilled, the methylol amine product of reaction I can not exist until reactions II a and II b are essentially complete.

Another point worthy of discussion in terms of the results of these measurements is the hydrothermal stability of formaldehyde tanned collagen. This latter subject has been discussed at length by numerous workers in the field, but has never been clearly resolved. Gustavson [9] has demonstrated that on tanning collagen in a 4 per cent formaldehyde solution the increase in shrink temperature is essentially independent of pH, if the pH is greater than 5.5. On the basis of these results he concluded that in spite of the increased uptake of formaldehyde at a higher pH, the extent of crosslinking did not change. This, of course, is in complete accord with the results presented here. Earlier Theis and Lams investigated the effects of the pH of tannage and the concentration of formaldehyde in the tanning bath upon the shrink temperature

of collagen [10]. These workers found that as the pH of tannage is increased from very low values (approximately pH 1), the shrink temperature increases until it approaches a nearly constant maximum value. The pH at which the shrink temperature levels off is a function of the formaldehyde concentration. With higher formaldehyde concentrations, this maximum is reached at a lower pH. Their data indicates that with 0.25 per cent formaldehyde, the maximum is attained at pH 4.5 to 5.5, and with 1 per cent formaldehyde, the pH for the maximum is approximately 4. This agrees very well with the pH at which crosslinking is complete. With 0.30 per cent formaldehyde the pH is 4.6 to 5, and with 1 per cent it is 3 to 4. (Table I and Figure 4). These results effectively confirm the argument that the increase in hydrothermal stability (on tanning with formaldehyde) is due primarily to the formation of crosslinks, and establish that maximum stability is attained only when crosslinking is complete.

Summary

The stress-strain behavior of thermally contracted formaldehyde tanned collagen has been investigated and the data treated in terms of the kinetic theory of rubber elasticity. Analysis of the data for collagen tanned at various pH's with different concentration formaldehyde solutions reveals:

(a) That formaldehyde introduces a maximum of 2 to 3.5 crosslinks per fundamental structural unit of collagen (M.W. = ca. 55,000).

(b) That only a portion of the total formaldehyde which is bound by collagen is utilized for the formation of crosslinks.

(c) That only about $1/7$ to $1/8$ of the side chain amino groups of collagen take part in the crosslinking reaction.

and(d)That those amino groups which do take part in the reaction apparently react preferentially with the formaldehyde.

The results of these physical measurements are in accord with the known organic chemistry of this reaction.

The relation between the shrink temperature and crosslinking has also been discussed, and it has been shown that the increase in hydrothermal stability is a direct consequence of the crosslinking reaction.

Acknowledgment

The authors would like to express their appreciation to Dr. J. H. Highberger for his helpful suggestions in the conduct of the work and in the preparation of this manuscript.

References

1. N. M. Wiederhorn and G. V. Reardon, *J. Polymer Sci.* in press.
2. C. E. Bresler, P. A. Finogenov, and S. V. Frenkel. *Reports Acad. Sci. (U.S.S.R.)* **72,** 555 (1950).
3. H. Fraenkel Conrat and H. S. Olcott. *J. Amer. Chem. Soc.* **70,** 2673 (1948).
H. Fraenkel Conrat and D. K. Mecham. *J. Biol. Chem.* **177,** 477 (1948).

4. L. R. G. Trelour. The Physics of Rubber Elasticity Oxford Press.
5. J. H. Highberger and C. E. Retzsch. *J. Amer. Leather Chem. Assoc.* **34,** 131 (1939)
6. J. H. Highberger and J. S. Salcedo. *J. Amer. Leather Chem. Assoc.* **35,** 11 (1940)
7. N. M. Wiederhorn and G. V. Reardon. Unpublished results.
8. J. H. Highberger. *J. Amer. Leather Chem. Assoc.* **42,** 493 (1947).
9. K. H. Gustavson. *J. Amer. Leather Chem. Assoc.* **43,** 744 (1948).
10. E. R. Theis and M. M. Lams. Unpublished data cited by G. D. McLaughlin and E. R. Theis. The Chemistry of Leather Manufacture P 355 Reinhold Publ. Co. (1945).

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Discussion

Joseph R. Kanagy (Silver Spring, Md.): I would like to ask Dr. Wiederhorn whether there is a possibility that the co-valent bonds are formed during the shrinkage process?

N. M. Wiederhorn: That, of course, is something which we had not investigated. The possibility of the co-valent bonds being formed during the shrinkage process, however, does not seem to me to be quite right. The reason is that there are soluble forms of collagen which can be denatured and still retain their solubility, whereas kangaroo tail collagen does not go into solution unless hydrolyzed.

Kanagy: During shrinkage a process seems to take place which causes it to contract as though it were rearranged. Isn't there a possibility that the co-valent bonds could be formed at that time?

Wiederhorn: The reason for the contraction of collagen during the shrinkage process is that in the native material we have a crystallized structure in an elongated form, and this is not a normal equilibrium state. The molecules would all like to be contracted. The molecule is held in the elongated form by salt bridges, and hydrogen and various other secondary bonds. When these bonds are broken the material can collapse into the contracted structure, which is the most natural structure. Also, now that the material is not held by these various secondary bonds, it is possible for it to swell to a much greater extent than in the native form.

Robert Stubbings (Bethlehem, Pa.): Did you tan specimens after shrinkage?

Wiederhorn: We did that and attempted to determine the stress-strain behavior, but the cross-linking was much greater than before shrinkage. As a matter of fact, it was so great we could not make measurements with our equipment. I doubt whether the material would have obeyed the rubber theory and, as such, our measurements would not have been valid; but it is much more cross-linked when tanned after shrinkage than before.

Stubbings: You attribute it purely to the mobility of those fibers?

Wiederhorn: Yes.

R. M. Lollar: What is your interpretation of the nature of the co-valent bonds which exist in collagen prior to your tannage, particularly with respect

to any structure like the Pauling structure, with the coiling of three chains between the helical structure?

WIEDERHORN: That is something I intended to mention. As far as our work is concerned, we cannot infer anything concerning the nature of the cross-links. It could be an amide cross-link or an ester cross-link or sulfur—sulfur bond as found in keratin.

However, the number of amino acids which are involved in the cross-linking structure is extremely small. If we go through the calculations we end up with the number of cross-linking amino acids being only .15 per cent of the total number present. So it would be very difficult to detect the exact chemical bond involved in the crosslink.

As to the nature of this, in terms of the Pauling structure, I do not see where there is any discrepancy here because Pauling says nothing about the long range structure. He confined himself to the short range structures, and completely ignored the long-range order observed in collagen.

LOLLAR: Might it not, however, be logical to assume that these cross-links which are formed are probably between the three chains in the same helix rather than between different helices, from structural factors?

WIEDERHORN: Concerning the three chains in the same helix, in a unit 640 angstroms in length, each chain, would have a molecular weight of 20,000. So that if the cross-links were between the three chains in the same helix we would end up with a molecular weight between cross-links of approximately 20,000. Consequently I believe that the cross link is at the end of the helix and there might be a deviation in the structure where the three chains run together. I feel the structure may involve two chains running down and one up, so that the long chain actually has an "S" shape.

THOMAS C. THORSTENSEN, (Baltimore, Md.): How did you measure the volume fractions?

WIEDERHORN: They were determined by soaking the sample for a period of time before the measurement was made. Then the stress-strain measurement was made and sample cut from the clamps. Then, having cut the samples from the clamps, the swollen sample was weighed and then dried by treatment with acetone, P_2O_5, and in an oven at a temperature of 100 degrees centigrade. The completely dried material was weighed again. From the dry weight, the swollen weight, the density of the swelling medium and the density of the dry collagen, which we assume to be 1.33, we were able to calculate the volume fraction.

THORSTENSEN: Your molecular weights are slightly smaller than you expected, by a factor of 10 per cent, and I wondered whether the apparent difference could be due to error in the volume fraction?

WIEDERHORN: This could be due to errors in the volume fraction or errors in the technique. We have a 10 per cent standard deviation so that our figure of 57,000 could be really anything from about 45,000 to 70,000. It is just nice that it came out 57, which is close to the 60.

STUBBINGS: If you shrink the specimens for various lengths of time you get more and more degradation or breakdown. Does that effect the cross-link picture? Where did you stop the shrinking process and make your measurements?

WIEDERHORN: You are perfectly correct. We heated some water to boiling, immersed the tendons, and it took a minute or two for the shrinkage to take place completely. We then took the samples out and plunged them into cold water. If you continue the treatment at high temperatures for any definite length of time, you get hydrolysis and the molecular weight goes up. We intend in the future to make a study of the hydrolysis by this method.

LOLLAR: Do you think it is probable that any co-valent bonds are broken in the shrinkage at 100 degrees? I am thinking particularly of the diminution one gets in the shrinking force when using a forced shrinkage meter, which occurs at around 85 or 90 degrees centrigrade in a neutral solution.

WIEDERHORN: I am not familiar with that type of measurement.

LOLLAR: What happens is this: As you increase the temperature on a tendon, as the sample starts to shrink at around 64, forces evolve; and as you reach a temperature of around approximately 85 or 90 degrees centigrade the force then drops off again.

Also, I found this to be true: That before you reach 85 or 90 you can cool the fiber down and come up again on much the same curve that you came up the first time; but when you go over 90 and the forces drop off, when you cool it there is at least a long hysteresis, if not a permanent change in the form of the forced temperature curve.

WIEDERHORN: I believe that could be due to one or two reasons: Either there could have been a continual hydrolysis, depending on the period of time—

LOLLAR: A half hour.

WIEDERHORN: There might have been considerable hydrolysis on going from 60 to 85 in a half hour. Also at a higher temperature the samples will swell to a greater extent and the increased swelling of the sample will lower the tensile stress necessary to maintain it at a constant length. It could be a combination or one of the two. That would be just my guess.

Extraction of Tannin and Dihydroquercetin From Douglas Fir Bark

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The Douglas fir tree grows in widely separated areas with extremely varied climatic conditions, such as exist between British Columbia and New Mexico.

It thrives in areas with excessively humid winters and excessively dry summers. With the exception of the redwood, the Douglas fir is the most gigantic tree of the Pacific forests. It reaches a hight of 180 to 200 feet, a diameter of 3.5 to 6 feet, and a maximum age of about 1400 years. The tree has a thick corky bark, which contains a rich supply of protective waxes, antioxidants, tannin and like preservatives [4, 6, 7]. Sudworth of the United States Forest Service has mentioned that some trees contain bark 18 to 24 inches in thickness [8].

Douglas fir is the major lumber, plywood, and pole and piling species in the United States. The annual production of Douglas fir lumber in the states of Oregon and Washington alone is more than 10 billion board feet. Based on this cut of 10 billion board feet and on an approximation of 500 pounds of bark from each thousand board feet of lumber [10], the potential annual supply of Douglas fir bark is about 2.5 million tons.

Douglas fir sawmills, plywood plants, and pole peeling plants accumulate large quantities of bark waste, most of which at present is disposed of as a lowgrade fuel or burned at the plant in bark burners. Some mills have as much as 50 tons of bark each day. It may be separated mechanically into cork flakes, short needle-like bast fibers, and an amorphous fine powder. On the other hand, it may be leached to recover certain chemical constituents. This report is concerned with the latter treatment.

The variation in yields of extractive products is related to both the height of the bark from the ground and the age of the tree. From old trees, the bark near the ground is lowest in tannin content and highest in wax and dihydroquercetin content, while bark from young trees contains the most tannin and the least wax. Bark from the top of the trees contains more tannin than bark from the base [4].

Recent analyses by the Oregon Forest Products Laboratory of Douglas fir bark from sawmills in different localities are given in Table I. The logs from which these samples of bark were taken had not been stored in water but the bark, in some cases, separated from the logs through the action of biological agents. For example, the 500 pounds of bark from Sweet Home, Oregon completely separated from the logs at the truck unloading platform. The data show that a yield of 146 to 200 pounds of tannin, 130 to 204 pounds of wax, and 80 to 152 pounds of dihydroquercetin may be expected from a ton of sound sawlog bark. In the conventional hide powder method for tannin analysis, a part of the dihydroquercetin appears as tannin, causing an overlap in the yields of these two water soluble constituents. An analysis of the tannin content in one lot of bark removed by a commercial hydraulic barker from logs ranging from 16 to 24 inches in diameter gave a 12.25 per cent yield of tannin by weight. Hand-peeled bark from 32 to 43 year old logs for poles and piling averaged a 9.0 per cent tannin content, and gave an extract of 52 per cent purity, which is the ratio of tannin to soluble solids

multiplied by 100. This bark was removed from the poles by the operator during the winter months of 1949–1950 but no further information concerning the condition of the bark was supplied. Since the trees in this young age group contain immature bark, the tannin extracts are low in purity because of the soluble carbohydrate content. A tannin raw material should have at least 7 per cent tannin content to warrant commerical extraction where the tannin is the sole product.

TABLE I

Analyses of Douglas Fir Bark from Sawlogs
(Percentages based on oven-dry weight of bark)

Source	Tannin	Wax	Dihydroquercetin
	Per Cent	Per Cent	Per Cent
Rockport, California	8.8	6.5	6.0
Taos, New Mexico	13.6	9.2	7.6
Fall Creek, Oregon	7.3	10.3	4.0
Mollala, Oregon	8.1	8.1	5.5
Corvallis, Oregon	10.0	7.4	6.0
Sweet Home, Oregon	8.8	6.7	5.7

Tannin materials of vegetable origin are critical in the production of leather, petroleum, and other industrial products. Suitable domestic sources to aid in meeting the needs of industry are being sought from native forest resources. Douglas fir tannin compares favorably with quebracho tannin for all of the major industrial uses, and it has been used for many years in leather making at the Muir-MacDonald Tannery at Dallas, Oregon. Dr. S. T. Tu of the B. D. Eisendrath Memorial Laboratory concluded from his tests on Douglas fir tannin extract that it is comparable to quebracho tannin. He reported that "the leather produced was full, firm and had an agreeable tan color. The tannin fixation, shrinkage temperature, and other characteristics of the leather all revealed that Douglas fir tannin resembles quebracho tannin." He also found that it could be blended with other tannin extracts [9].

From 40 to 50 per cent of the tannin consumed in this country is used by the petroleum industry for controlling the consistency of oil-well drilling muds. Two industrial laboratories have reported that Douglas fir bark tannin compares favorably with quebracho tannin for this use.

The Bureau of Mines' Laboratory at Tuscaloosa, Alabama, was interested in finding a material that would be beneficial for the concentration of low grade iron ores. Their tests on Douglas fir bark tannin extract indicate that it is as efficient as quebracho tannin for this purpose.

Dihydroquercetin has been obtained in yields of more than 7 per cent from some Douglas fir barks submitted to this Laboratory. The highest concentrations were found in the cork fraction of the bark; some Douglas fir cork

has been found to contain more than 20 per cent by weight of dihydroquercetin [3].

Dihydroquercetin is a tasteless, white crystalline compound with a melting point of 252 to 253° C. It appears to be nontoxic, possesses pharmacological properties, and is an effective antioxidant for the prevention of rancidity in fats, oils, and dairy products [7]. It combines with hides to form a white leather product. The solubility of dihydroquercetin in water is 9.3 per cent at 100° C., and only 0.51 per cent at 15° C. This flavanone differs chemically from the naturally occurring yellow coloring matter, quercetin, only in that it has two more hydrogen atoms in the molecule than quercetin. Dihydroquercetin may be converted in part into quercetin during the vacuum evaporation of Douglas fir bark tan liquors. It is soluble in sodium bisulfite solutions, whereas quercetin is insoluble.

Processing at tannin and dihydroquercetin extraction plants will include drying of the bark before storage, bark grinding, leaching, and evaporation of the liquors.

Douglas fir wax is a valuable product with a melting point of about 58 to 60°C. It is harder than beeswax but not as hard as carnauba wax. Its physical properties can be easily modified, and melting points higher than those of carnauba wax have been obtained.

Recent interest in the commercial extraction of waxes, tannin, and dihydroquercetin from Douglas fir bark indicates the need for further laboratory studies. Several integrated extraction procedures for the recovery of wax, tannin, and dihydroquercetin from Douglas fir bark, however, appear feasible. Among them are the following:

Method 1. The ground bark is first extracted with benzene or a chlorinated aliphatic hydrocarbon solvent to remove the waxes. The dihydroquercetin is then recovered from the wax-free bark by extraction with a lower alkyl ether. Finally, the tannin is extracted with hot water from the bark residue.

Method 2. The ground bark is extracted with an appropriate solvent to remove the waxes. The bark residue is then extracted countercurrently with hot water to remove tannin and dihydroquercetin. Subsequent separation of dihydroquercetin from the tannin is effected by means of a lower alkyl ether, such as diethyl ether or diisopropyl ether. For this step, the tan liquor is evaporated to a small volume or to a dry powder. As the tannin is less soluble in diisopropyl ether than in diethyl ether, the former solvent will give relatively pure dihydroquercetin. A longer extraction period, however, is required because of the lower degree of solubility of dihydroquercetin in diisopropyl than in diethyl ether.

Method 3. The ground bark is extracted countercurrently with hot water to remove tannin and dihydroquercetin. The residue is then extracted with an appropriate solvent to remove the waxes.

Method 4. The ground bark is extracted with a constant boiling mixture of alcohol-benzene. With this solvent, the waxes, dihydroquercetin, tannin,

and phlobaphene are largely removed from the bark in one operation. After removing the alcohol-benzene mixture from the extract, the waxes are extracted with hot benzene and the dihydroquercetin with ether. The tannin and phlobaphene, which remain, are then separated by dissolving the tannin in hot water.

A bark sample, ground to pass a $\frac{1}{4}''$ screen and retained on a $\frac{1}{16}''$ screen, was extracted by Methods 1, 2 and 4 and the yields of waxes, tannin, and dihydroquercetin by each method are shown in Table II. Among the methods tried, Methods 2 and 3 appear to be the most practical for the commercial production of wax, dihydroquercetin, and tannin. Dihydroquercetin obtained from the bark by Method 4 was contaminated with red resinous material and was difficult to purify.

TABLE II

Yields of Extractives by Different Methods of Extraction

	Method 1	Method 2	Method 4
Benzene soluble waxes, Per cent	7.29	——	6.0
Dihydroquercetin, Per Cent	9.82	9.70	7.9
Total hot water solubles (tannin, etc.) Per Cent	5.67	5.61	7.0

Effect of Drying Bark

Improper curing of chestnut oak, tanoak, and hemlock barks contribute to low tannin yields [2]. When Douglas fir logs are left lying on the ground in the woods exposed to wet weather or when the logs are stored in mill ponds, the bark shows definite signs of deterioration by biological action and, frequently, wood and bark become separated. Such bark generally has a moisture content between 30 to 40 per cent. After drying, however, the bark may be stored commercially under cover without deleterious effects. Previous tests on the effect of drying sound Douglas fir bark out-of-doors on the yield of tannin showed an increase in tannin in the dry bark over that in the bark before drying [5]. Therefore, additional tests were made to ascertain the comparative yields of tannin from freshly collected, sound bark and from the same bark after drying.

In May, 1951, samples of bark were taken from four trees soon after felling. Two of the trees were 50 years old, one 60 years old, and one 130 years old. Conventional analyses for water soluble extractives were made on representative samples of the ground barks from each tree before and after drying. The data are summarized in Table III. Sample 1 was from a 50-year old tree, 14.5 inches in diameter. Sample 2 was from a 130-year old tree, 40 inches in diameter. Sample 3 was from a 50-year old tree, 23 inches in diameter. Sample 4 was from a 60-year old tree, 21 inches in diameter.

TABLE III

The Effect of Air-Drying Bark on Tannin Yield
(Percentage based on oven-dry weight of bark)

Bark Sample	Moisture	Total Solids	Soluble Solids	Tannin	Nontannin
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
1. At time of collection	30.85	16.45	14.45	5.49	8.96
Dried 6 days in sunlight	20.06	16.99	15.47	6.43	9.04
2. At time of collection	19.93	25.15	23.46	15.53	7.93
Dried 6 days in sunlight	5.85	31.65	28.29	18.36	9.93
3. At time of collection	32.66	17.65	15.22	8.40	6.82
Dried 6 days in sunlight	16.05	18.81	16.85	10.16	6.69
4. At time of collection	22.82	16.36	13.99	7.69	6.30
Dried 6 days in sunlight	7.32	18.23	16.87	8.93	7.94

The bark samples all showed an increase in tannin and other water soluble constituents upon drying out-of-doors. The largest increase was found in the bark from the 130-year old tree and the least in the bark from the 50-year old trees. Bark from very young Douglas fir trees is immature and contains a high proportion of nontannins of a carbohydrate nature.

Experiments were also performed to ascertain the effect of artificial drying on the yield of tannin from Douglas fir bark. For this purpose, about seventy-five pounds of bark were taken from a living Douglas fir tree estimated to be about 120 years old. The bark was ground immediately after collection in a hog mill with a 1″ screen. Samples of this bark were dried in a Dietert Moisture Teller with forced hot air at temperature from 150 to 205° F. for one hour. After drying, the samples were ground to pass a 20-mesh sieve and then analyzed for tannin content. The data are shown in Table IV.

TABLE IV

The Effect of Artificial Drying of Bark on Tannin Yield
(Percentage based on oven-dried weight of bark).

Sample	Moisture at Time of Analysis	Total Solids	Soluble Solids	Tannin	Nontannin
	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
Original bark before drying	43.29	17.56	15.65	9.69	5.96
Dried 1 hour at 150° F.	9.19	17.15	15.65	10.15	5.50
Dried 1 hour at 175° F.	6.45	17.26	15.95	10.37	5.58
Dried 1 hour at 205° F.	5.20	17.95	15.29	9.51	5.78

Artificial drying of the bark for one hour with forced hot air at 150° F. to 175° F. caused a slight increase in tannin content over the freshly cut, undried bark. The same bark dried for six days in the sunlight to a moisture content of 6.44 per cent revealed an increase in tannin content from 9.69 per cent in the undried bark to 10.36 per cent in the dry bark.

Countercurrent, Batch Extraction for Tannin and Dihydroquercetin

Bark Raw Material

Experiments were carried out on four different lots of bark with the view to ascertaining the optimum conditions for tannin and dihydroquercetin extraction. Representative samples of fresh and spent barks were taken systematically from each lot of bark during the course of the extraction tests and were extracted in the tannin extraction apparatus recommended by the American Leather Chemists Association. The extracts were then analyzed in accordance with the official methods of the Association [1]. The results are given in Table V. It was found that the highest yield of tannin was obtained by using an extraction time of between 8.5 to 9 hours when the analytical bark samples were ground to pass a 20-mesh sieve.

TABLE V

Chemical Analysis of Bark
(Percentage based on oven-dry weight of bark)

	Lot 1	Lot 2	Lot 3	Lot 4
Total solids, Per cent	21.20	16.90	13.24	17.60
Soluble solids, Per cent	19.46	14.93	12.55	16.75
Insolubles, Per cent	1.74	1.99	0.67	0.85
Tannin, Per cent	11.10	8.88	7.50	9.10
Non tannins, Per cent	8.36	6.05	5.05	7.65
Dihydroquercetin, Per cent	small	7.70	6.68	6.05
Moisture, Per cent	12.46	———	26.59	13.55
Purity (tannin/sol. sds.)	57.0	59.5	59.8	54.3

The 1200 pounds of bark in Lot 1 was obtained from the covered storage shed at the Muir-MacDonald Tannery in Dallas, Oregon. This bark was 1.5 to 2 inches thick. Part of the bark, 1a, was ground in a hog equipped with a one inch screen, the rest, 1b, in the same hog with a .5 inch screen.

The 1500 pounds of bark in Lot 2 was obtained from sawlogs at Florence, Oregon, in November, 1950. This bark was wet and, due to weathering and decay, had separated from the logs at a truck-unloading zone. The trees had been cut and the logs had lain on the ground in the woods for some time. The bark was ground in a hog equipped with a screen with .5 inch diameter holes, and then dried in a dry-kiln on specially built screen racks before extraction.

Bark in Lot 3 was a screened fraction taken from Lot 2 bark that had been extracted with benzene to remove the wax. This fraction passed a screen with .25 inch openings and was retained on a No. 18 sieve.

Bark in Lot 4 weighed about 1500 pounds and was obtained from sawlogs at a sawmill ten miles north of Corvallis, Oregon. The bark was hand peeled in May 1951 from recently cut trees ranging from 80 to 170 years in age and

from 23 to 38 inches in diameter. The bark was dried outdoors for three weeks to an average moisture content of 13.5 per cent. It was then ground in a hog equipped with a screen with one-inch diameter holes. The ground bark was thoroughly mixed on a cement floor and placed in air-tight containers to maintain constant moisture until extracted.

Samples of each of the aforementioned barks were taken for sieve and tannin analysis. The sieve analyses are given in Table VI.

TABLE VI

Sieve Analysis of Barks

Passing	Retained on	Lot 1		Lot 2	Lot 3	Lot 4
		a	b			
		Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
——	½"	5.8	0.0	0.0	0.0	4.5
½"	4-mesh	44.7	8.2	3.7	9.9	10.8
4-mesh	6-mesh	13.2	15.9	15.0	23.8	17.3
6-mesh	10-mesh	13.7	22.3	25.9	43.3	15.4
10-mesh	20-mesh	8.5	20.5	16.4	12.6	9.9
20-mesh	60-mesh	9.8	24.3	24.7	8.3	8.3
60-mesh	100-mesh	2.4	4.7	7.7	1.5	2.6
100-mesh	200-mesh	1.3	2.3	4.7	0.5	0.8
200-mesh	——	0.6	1.8	2.0	0.1	9.4

Analysis for dihydroquercetin.

For the estimation of the dihydroquercetin content of the barks, the samples were extracted, as for tannin, in the tannin apparatus approved by the American Leather Chemists Association [1]. Aliquot quantities of the aqueous extract were then shaken with alcohol-free ethyl ether. Reproducible results were obtained by shaking a 50 ml. aliquot of the liquor with four succesive 25 ml. portions of ether in a separatory funnel. Usually, the first extraction with ether removed 90 per cent of the total dihydroquercetin present in the liquor. The ether was evaporated and the residue dried at 105° C., cooled and weighed. About 95 per cent of the orange colored dry residue was dihydroquercetin. A white, pure product was obtained by decolorization with charcoal in a boiling water solution and subsequent crystallization.

Bark Extraction.

Extraction of the tannin from Douglas fir bark in an autoclave at high temperature was found to lead to the formation of a large amount of insolubles. In the present study, therefore, the bark, with or without wax removed, was extracted countercurrently with hot water in wooden barrels, arranged in batteries of four or five. Each barrel was provided with a false bottom constructed of a 14-mesh copper screen. The bottom of each barrel was provided with a pipe and valve for draining off the liquor.

A series of extractions on a particular lot of ground bark began with one barrel containing fresh bark and hot water. At the end of the leaching period,

the liquor was drained off and added to a second barrel with fresh bark. This method was used for the purpose of determining the concentration of the liquor at the end of four or five successive leachings of fresh bark, as shown in Table VII. The leaching series and conditions are shown in Table VIII.

TABLE VII

Total Solid Content of Tan Liquor From Five Successive Leachings of Fresh Bark

Bark Lot No.	Leaching Series No.	Total Solids in Liquor
		Per Cent
1a	8	6.18
1b	13	5.53
2	10	2.93
3	16	2.77
4	17	3.33

Fresh bark introduced into the system was leached by the liquor that had been used previously to leach the bark in all the other barrels in the extraction unit. The last leaching of the spent bark was made with fresh hot water. This sequence was continued until the leaching system reached equilibrium. Normally, equilibrium was reached after nine or ten barrels of fresh bark were introduced. Figure 1 shows the countercurrent extraction system with five extraction barrels after equilibrium conditions were established.

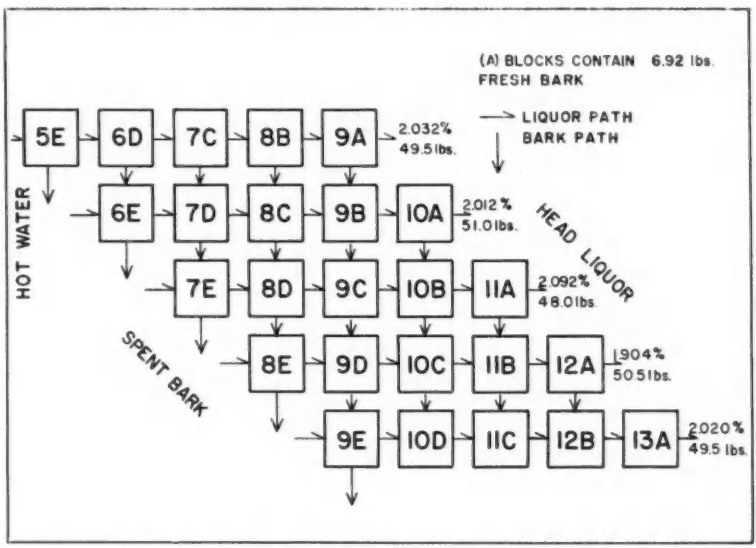

FIGURE 1.—Countercurrent Extraction of Douglas Fir Bark, Series No. 18.

TABLE VIII

Leaching of Douglas Fir Bark

Leaching series No.	Bark Lot No.	Number of runs in series	No. of barrels in battery	Temperature head to tail	O. D. bark per barrel	Water in barrel	Liquor drained for each pound bark	Leaching time per leach	Total leaching time for all leaches
				°F.	Pounds	Pounds	Pounds	Hours	Hours
4	1a	6	4	135, 150, 170, 194	9.63	66	5.4	2	8
5	1a	5	5	135, 150, 170, 194, 194	9.63	66	5.4	2	10
6	1a	5	5	135, 150, 170, 194, 194	9.63	66	5.4	1	5
7	1a	5	4	135, 150, 170, 194	9.63	66	5.4	1	4
8	1a	5	5	149, 170, 190, 200, 200	9.74	66	5.3	3	15
13	1b	5	5	149, 170, 190, 200, 200	8.16	60	7.35	3	15
9	2	5	5	149, 170, 190, 200, 200	5.89	56	9.5	3	15
10	2	5	5	149, 170, 190, 200, 200	7.57	56	7.4	3	15
11	2	5	5	149, 170, 190, 200, 200	8.00	60	7.5	2	10
12	2	5	4	149, 170, 190, 200, 200	8.08	60	7.4	3	12
16	3	5	5	165, 183, 198, 205, 205	6.61	56	8.5	3	15
17	4	5	5	147, 167, 196, 210, 210	6.92	60	7.02	3	15
18	4	5	5	147, 167, 196, 210, 210	6.92	60	7.18	4	20
19	4	5	5	147, 167, 196, 210, 210	6.92	60	7.22	2	10

Table VIII illustrates the data recorded in the leaching of the four lots of bark under different experimental conditions. The temperature of the liquor was lowest on the fresh bark (head) and highest on the spent bark (tail). This temperature gradation was maintained to minimize discoloration of the tannin, condensation of the tannin to insoluble phlobaphene, and oxidation of dihydroquercetin to quercetin. As indicated, several runs were made in each series under different experimental conditions.

Samples of the spent bark and tannin liquor were analyzed by the methods of the American Leather Chesmists Association. The amount of tannin and dihydroquercetin recovered from the bark was calculated from the weight of the tannin liquor and the amount of these constituents in this liquor. Based on this calculation and on the tannin and dihydroquercetin content of the fresh bark, the efficiency of extraction was calculated for each particular set of conditions. Table IX shows the percentage of the various constituents extracted from the bark and Table X the efficiency of extraction.

TABLE IX

Leaching of Douglas Fir Bark
(Per cent yield from bark)

Lot No.	Series No.	Total Solids	Soluble Solids	Insolubles	Non-tannin	Tannin	Dihydroquercetin
		Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent
1a	4	13.12	12.64	0.48	5.72	6.97	——
	5	14.90	——	——	——	——	——
	6	13.99	——	——	——	——	——
	7	12.15	——	——	——	——	——
	8	15.17	14.96	0.21	6.72	8.25	——
1b	13	15.88	14.27	1.61	6.10	8.09	——
2	9	13.31	12.26	1.05	5.23	7.13	5.05
	10	12.58	11.39	1.19	4.88	6.51	4.65
	11	11.25	10.20	1.05	4.35	5.85	3.90
	12	11.36	10.40	0.96	4.53	5.87	4.20
3	16	11.18	11.01	0.17	4.74	6.27	4.54
4	17	13.34	12.78	0.56	5.83	6.95	3.23
	18	14.51	14.22	0.29	6.68	7.54	3.38
	19	12.57	——	——	——	——	——

In each series, a comparison was made of the yield of extractives as determined by an analysis of the spent barks and that by an analysis of the tan liquors recovered from the bark. No material difference in yields was found by the two methods. As an example, in series 9 the total solids extracted were 13.31 per cent and the residual hot water extractive in the spent bark was 3.96 per cent. The sum, 17.27 per cent, is comparable to 16.90 per cent hot water extractives found in the unextracted bark.

TABLE X

Efficiency of Leaching Douglas Fir Bark

Lot No.	Series No.	Efficiency on Basis of Total Solids Content	Efficiency of Tannin Extraction	Efficiency of Dihydroquercetin Extraction
		Per Cent	Per Cent	Per Cent
1a	4	61.9	62.8	——
	5	70.3	——	——
	6	66.0	——	——
	7	57.3	——	——
	8	71.6	74.3	——
1b	13	74.9	72.9	——
2	9	78.8	80.3	65.6
	10	74.4	73.3	60.4
	11	66.5	65.9	50.7
	12	67.2	66.1	54.6
3	16	84.4	83.6	68.0
4	17	75.8	76.4	53.4
	18	82.4	82.9	55.9
	19	71.4	——	——

Summary of Results

The data indicate that about 80 to 85 per cent of the tannin will be extracted from the bark in 15 hours total leaching time in a countercurrent, batch extraction unit containing five leachers when the water to bark ratio is sufficient to completely cover the bark. Because of the lower solubility of the dihydroquercetin and because it is present largely in the cork fraction of the bark, the efficiency of the dihydroquercetin extraction under the same conditions will be only 55 to 65 per cent. Efficiency of extraction increased with increased leaching time. In tannin extraction, the efficiency increased from 71 per cent with two hours leaching time per leacher to 82 per cent with four hours leaching time per leacher. Five leachers in the countercurrent extraction system gave greater efficiency than four leachers. The total solids content of the tan liquor from the bark was approximately 2.0 per cent. Removal of the wax from the bark with benzene extraction prior to tannin extraction with hot water, gave the most efficient extraction of total solids, tannin, and dihydroquercetin.

The reducing sugar content of the Douglas fir bark tannin extracts was 18.1 to 18.4 per cent of the oven-dry weight of the total solids. By hydrolysis, this was increased to 29.0 per cent of the oven-dry weight of the total solids. The insoluble matter in the evaporated tannin extracts was a mixture of phlobaphenes, quercetin or dihydroquercetin. For example, the tannin extract from the bark in Lot 4, upon evaporation to approximately 40 per cent total solid content, gave a large crop of dihydroquercetin crystals upon standing. Analysis of the phlobaphene for methoxyl group content showed

1.34 per cent methoxyl. Purity of the tannin extracts varied with the condition of the bark prior to extraction. A purity of 55 to 60 per cent tannin content apparently may be considered normal for tannin extracts from properly cured, sound Douglas fir bark. For maximum yield of tannin and purity of the tannin extract, the bark must be removed from the logs and dried soon after the trees are felled.

Literature Cited

1. American Leather Chemists Association. "Methods of Sampling and Analysis." Cincinnati, Ohio (1946).
2. Beebe, C. W., Cordon, T. C. and Rogers, J. S., *J. Amer. Leather Chemists Assoc.* **41**, 161, (1946).
3. Hergert, H. and Kurth, E. F., *Tappi*, **35**, No. 2, 59 (1952).
4. Hubbard, J. K. and Kurth, E. F., *J. Amer. Leather Chemists Assoc.*, **44**, 604 (1949).
5. Kurth, E. F., Hubbard, James K., and Gekeler, Maurice., *Leather and Shoes*, **118**, No. 20, 22 (1949).
6. Kurth, E. F., and Kiefer, H. J., *Tappi*, **23**, 183 (1950).
7. Kurth, E. F., and Chan, F. L., *Jour. Amer. Oil Chemists' Soc.* **28**, No. 10, 433 (1951).
8. Sudworth, G. B. "Forest Trees of the Pacific Slope." Forest Service, U.S.D.A., Government Printing Office, Washington, D. C. 1908.
9. Tu, S. T. Private Communication
10. Voorhies, G., "An Inventory of Sawmill Waste in Oregon." Engineering Experiment Station Oregon State College, Corvallis, Oregon. Bulletin 17 (July 1942).

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Tennessee Valley Oak Bark as a Source of Tannin*

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During most of the present century, chestnut wood has been the principal source of domestic tanning extract in the United States. The blight has now killed practically all the commercially available chestnut trees in this country and after a few years, domestic chestnut tanning extracts will not be available.

This condition has led to many investigations of materials to replace chestnut and to make this country less dependent upon foreign sources. The Eastern Regional Research Laboratory of the United States Department of Agriculture has published reports on Pacific Coast hemlock bark [1], Sitka spruce bark [2], tara pods [3], Florida scrub oak bark [4], sumac leaves [5] and canaigre roots [6]. In addition to these published reports, this Laboratory is cooperating with the lumbering and pulping industries on the utilization of waste materials

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from these industries for the production of tanning extracts. One of these projects has been a collaboration with the Forestry Relations Department of the Tennessee Valley Authority on the utilization of waste oak slabs.

Oak bark is one of the oldest materials used in tanning and is generally regarded as producing a high grade leather. A well-prepared oak bark extract reasonably priced would probably be readily accepted by the tanning industry.

Bailey and Cummings [7] and Snow and Bailey [8] have reported on the amount of oak slabs available in the Tennessee Valley and some of the factors involved in the collection of the bark. They found that there are potentially available annually 128,000 cords of oak slabs and that the future supply is assured as the present rate of lumber production is favorably balanced by volume growth in saw timber stands. They have also given the results of laboratory extraction and tanning tests. The extraction tests were made with a composite mixture of bark and wood as it occurs in the slabs. This had a tannin content of 3.9 per cent and gave a liquor with a purity of 45. It is doubtful whether this proposed method of extraction of material with such a low tannin content would be feasible. Further, the purity is much lower than is desired. Another factor to be considered is that the wood in the mixture, which would be lost in this process, has a potential value as pulp.

Considerable work has been done by investigators of the TVA, using the method proposed by Calderwood and May [9] for the utilization of bark and wood mixtures. This consists of suitable chipping of the material, screening into several size groups and segregation by air flotation of each of the resulting groups according to density. The term "segregation" is used for the sorting into constituents of material consisting merely of a mixture. The term "separation" is used where the constituents are joined and must be separated by cleavage. They have found that the average specific gravity of wood from 3 species of oak is 0.66 and that of bark from the same species is 0.84. The difference in specific gravity is sufficient to make segregation by air flotation feasible but thorough classification into size groups is required before flotation.

Segregation of Bark from Wood and Leaching of Bark

Several hundred pounds of oak waste were chipped by TVA investigators in a manner previously found most suitable for the subsequent segregation procedure. The waste consisted of about equal parts of black oak, *Quercus velutina*, and scarlet oak, *Q. coccinea*, with some southern red oak, *Q. falcata*. Three types of waste were used, designated in the lumber industry as slabs, edgings and round wood. The chipped slabs before segregation consisted of about 42 per cent bark and 58 per cent wood. These were divided into the following groups: (1) that passing a 1-inch mesh screen but held by a ½-inch screen; (2) that passing a ½-inch screen but held by a ¼-inch screen; (3) that passing a ¼-inch screen but held by a ⅛-inch; (4) that passing a

1/8-inch screen but held by a 1/12-inch; (5) all material passing a 1/12-inch screen. Each group was divided into 2 fractions—a wood-rich fraction and a bark-rich fraction. For pulping purposes, little bark can be tolerated in the wood; therefore, this fraction was kept as pure as possible. All material containing 29 per cent or more of bark was placed in the "bark" fraction, thereby greatly diluting this fraction. The samples were sent to the Eastern Regional Research Laboratory for analysis and leaching tests. Table I shows the analyses of the segregated "bark" fractions of the various sizes from 3 types of waste material. This table also gives the analysis of pure wood chips to show the effect of excessive amounts of wood in the "bark" fraction.

TABLE I

Influence of Particle Size Upon Separation of Bark and Wood.
Composition of Bark-rich Fraction after Segregation.

Wood Waste	Bark Fraction		Tannin Analysis — Moisture-Free Basis				
	Particle Size	Bark Content	Total Extractive	Soluble Extractive	Soluble Non-Tannin	Soluble Tannin	Purity Basis S. E.
	Inches	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	
Slabs*	½ – 1	64	13.8	12.4	5.7	6.7	54.0
	¼ – ½	84	16.0	14.6	6.1	8.5	58.2
	⅛ – ¼	95	15.3	13.7	5.8	7.9	57.7
	1/12 – ⅛	84	12.7	11.4	5.0	6.4	56.1
	Less than 1/12	90	13.7	12.6	5.8	6.8	53.9
Edgings	½ – 1	65	13.8	12.2	5.6	6.6	54.1
	¼ – ½	84	15.7	13.9	5.9	8.0	57.5
	⅛ – ¼	92	14.5	13.3	5.6	7.7	57.9
	1/12 – ⅛	92	12.2	10.9	5.2	5.7	52.3
	Less than 1/12	90	14.0	12.9	5.6	7.3	56.6
Round Wood	¼ – ½	45	10.0	9.5	4.3	5.2	54.7
	⅛ – ¼	78	12.2	11.4	4.7	6.7	58.7
	1/12 – ⅛	52	8.7	8.3	4.4	3.9	47.0
	Less than 1/12	80	10.1	9.6	4.8	4.8	50.0
Wood Chips			8.5	8.0	4.8	3.2	40.4

*The mixture used consisted of approximately 42 per cent bark and 58 per cent wood before segregation.

As the segregation of wood and bark in the round wood was poor as compared with that from slabs of edgings, only the "bark" fractions from slabs and edgings were used for a leaching test. These were mixed in the proportions shown in Table II. A hand segregation test after mixing showed 72.4 per cent bark, as compared with the calculated 72.9 per cent.

A sample for a second leaching test was prepared by mixing in the proper proportions the three middle-size fractions shown in Table II. The large material was omitted because of the small proportion of bark, and the fine material because it might cause trouble in leaching.

TABLE II

Segregated Bark Fractions from Slabs and Edgings as Combined for First Leaching Test

Particle Size	Proportion of Total Material	Proportion of Bark in Sample	Proportion of Bark to Total Material
Inches	Per Cent	Per Cent	Per Cent
$\frac{1}{2}$ – 1	11	66	7.3
$\frac{1}{4}$ – $\frac{1}{2}$	42	74	31.1
$\frac{1}{8}$ – $\frac{1}{4}$	28	71	19.9
$\frac{1}{12}$ – $\frac{1}{8}$	6	71	4.2
Less than $\frac{1}{12}$	13	80	10.4
Total	100		72.9

For leaching, a countercurrent 8-vat system was used, in which the liquors were moved forward once an hour. A temperature of approximately 200° F. was used on the tail leaches, and the head liquor was taken off at about 140° F. Operation of the system was continued until equilibrium had been reached. Analyses by the Official Methods of the American Leather Chemists Association [10] were made of the original bark mixture, the liquor obtained, the spent material produced, and the liquid extract produced. The results of both these leaching tests are shown in Table III. A tannin recovery of 65 per cent was obtained in leaching the entire composited mixture, and 69 per cent was obtained in leaching the middle fractions. These results are promis-

TABLE III

Leaching Tests on Composite Bark Material

1. Extraction of Total Composited Bark Material

	Original Composite Mixture**	Equilibrium Head Liquor	Extract	Spent Material**
Total Extractive Per Cent*	13.3	2.7	50.9	5.8
Soluble Extractive Per Cent*	12.2	2.7	50.2	5.1
Insolubles in Extractive Per Cent	1.1	0.0	0.7	0.6
Soluble Nontannin Per Cent	5.7	1.4	25.5	2.2
Tannin Per Cent	6.5	1.3	24.7	2.9
Purity—basis Sol. Ext.	53.5	47.7	49.1	57.6

2. Extraction of Three Middle Bark Fractions Combined

Total Extractive Per Cent*	13.8	2.4	53.7	4.6
Soluble Extractive Per Cent*	12.6	2.4	52.4	4.1
Insolubles in Extractive Per Cent	1.2	0.0	1.3	0.5
Soluble Nontannin Per Cent	5.8	1.2	26.5	1.8
Tannin Per Cent	6.8	1.2	25.9	2.3
Purity—basis Sol. Ext.	53.5	50.0	49.5	55.9

*In liquors and extracts, these values are for total solids and soluble solids, respectively.
**Moisture-free basis.

TABLE IV

Analyses of Pure Oak Barks Collected from Eight Species of Oaks* in the Tennessee Valley Area

Species of Oak	Collection	Avg. Diam. B.H.	Analysis — Results on Moisture-Free Basis					
			Total Extractive	Soluble Extractive	Insolubles	Non-tannin	Tannin	Purity Basis Sol. Ext.
		Inches	Per Cent	Per Cent	Per Cent	Per Cent	Per Cent	
Quercus alba	1	19.6	10.3	10.0	0.3	3.9	6.1	58.9
White	2	18.4	12.3	12.0	0.3	5.4	6.6	55.0
	R**	——	——	12.7	——	4.8	7.9	62.2
	H						7	
Q. velutina	1	14.7	19.0	15.2	3.8	5.9	9.3	61.2
Black	2	20.7	20.3	16.7	3.6	7.4	9.2	55.1
	R	——	——	14.8	——	6.4	8.4	56.8
	H						6–12	
Q. falcata	1	12.1	15.7	14.4	1.3	4.5	9.9	68.6
Sou. Red	2	15.4	17.4	14.8	2.6	5.1	9.7	65.6
	R	——	——	14.4	——	5.3	8.7	60.4
Q. montana	1	23.6	28.3	24.9	3.4	9.6	15.3	66.5
Chestnut	2	19.5	28.9	27.4	1.6	11.4	16.0	59.1
	R	——	——	17.6	——	6.8	10.8	61.4
	H						8–14	
Q. borealis	1	13.2	11.4	10.4	1.0	5.0	5.4	52.1
Northern Red	2	16.8	13.2	12.0	1.2	5.6	6.4	53.3
	R	——	——	18.8	——	7.9	10.9	58.0
	H						5.5	
Q. marilandica	1	10.4	15.3	14.7	0.6	5.5	9.2	62.8
Black Jack	2	7.7	14.3	13.6	0.7	4.8	8.8	64.7
	R	——	——	11.8	——	4.1	7.7	65.3
Q. coccinea	1	11.9	14.3	12.7	1.6	5.6	7.1	56.1
Scarlet	2	20.8	19.1	17.8	1.3	7.2	10.6	59.5
	R	——	——	11.5	——	4.9	6.6	57.4
	H						7.7	
Q. stellata	1	10.2	12.5	12.1	0.4	4.7	7.4	61.4
Post	2	15.5	13.1	12.5	0.6	5.4	7.1	56.8
	R	——	——	11.0	——	7.9	3.1	28.2

*Each sample of bark analyzed was a composite of barks collected from 10 trees.
**"R" indicates data reported by A. Russell[11]; "H" indicates data reported by Harvey[12].

ing, but the yield is poor and the purity of the extract is too low for a satisfactory tanning material. The analysis of wood chips in Table I shows that the tannin content and purity of the wood are low and, therefore, the proportion of wood in the bark fraction must be cut down before it is satisfactory.

Another way to improve the tannin content and the purity would be to select raw materials in such a way that only barks of higher tannin content

and purity would be included and barks of low tannin content and purity would be excluded. The bark of chestnut oak, *Q. montana*, containing about 15 per cent tannin, was omitted from these tests because it is a well-established tanning material. The inclusion of as much bark as possible of this species would increase the value of the mixture.

To determine the tannin contents of oak barks from trees in the Tennessee Valley, a collection of bark was made from 8 of the predominant species. Each sample consisted of a composite collected from 10 trees of the species, taken from freshly cut trees of sawlog size. A strip was removed at breast height from the entire circumference of the tree. Analyses were made of the 8 samples, and a composite sample was made for a leaching test. Another collection of 10 samples taken in a similar manner was made at a later date. Analyses of these samples are given in Table IV, together with results obtained by Russell [11] and some given by Harvey [12]. It should be kept in mind that Russell's results were obtained on a sample from only one tree from each species. The data show that there is fairly close agreement between the different samples from each species.

For a leaching test, the barks were composited approximately in proportion to their relative occurrence in the Tennessee Valley. Table V shows the distribution of oak timber trees as determined by the Tennessee Valley Auhtority. Since all the species were not sampled, the 8 samples were composited in the following proportions to give as nearly as possible a representative sample: *Q. Alba*, 26 per cent; *Q. velutina* and *falcata*, 12 per cent each; *Q. montana*, 9 per cent; *Q. borealis*, 5 per cent and *Q. marilandica*, *coccinea* and *stellata*, 12 per cent each. By analysis, this mixture contained 8.6 per cent tannin with a purity of 58.7, as compared with a calculated value from the separate constituents of 8.6 per cent tannin and a purity of 58.3.

TABLE V

Distribution of Oak Species in the Tennessee Valley

	Per Cent
White Oaks – *Q. alba, prinus,* and *lyrata*	26
Black Oaks – *Q. velutina, falcata, palustris, pagodafolia*	24
Chestnut Oak – *Q. montana*	9
Northern Red Oak – *Q. borealis*	5
Other Oaks – *Q. marilandica, coccinea, stellata, nigra, laurifolia, shumardi*	36

The bark was ground in a Ball and Jewel Mill with a 1-inch screen. It contained quite a high proportion of both large pieces and fines and hence was not as suitable for leaching as a more uniform product. The leaching test was made in a similar manner to that of the preceding tests. A tannin

recovery of 72 per cent was obtained. Table VI gives the analysis of the original fresh bark, the spent material, the liquor obtained, and the extract made from it. It is believed that with material ground to a more uniform size a somewhat higher tannin recovery and an extract with a higher purity could be obtained.

TABLE VI

Extraction of Composite Sample of Pure Barks

	Fresh Bark	Spent Material	Liquor	Extract
Total Extractive, Per Cent*	15.8	4.4	1.2	31.2
Soluble Extractive, Per Cent*	14.7	3.9	1.1	31.0
Insolubles in Extractive, Per Cent	1.1	0.5	0.1	0.2
Nontannin, Per Cent	6.1	1.6	0.5	13.9
Tannin, Per Cent	8.6	2.3	0.6	17.1
Purity = Tan./S.S. x 100	58.3	59.2	55.1	55.0

*In liquors and extracts, these values are for total solids and soluble solids, respectively.

A tanning test was made with this extract. Pieces of steer hide— after liming, unhairing, fleshing, and partial deliming—were obtained from a commercial tannery. They were placed in a liquor of 0.5 per cent tannin. This liquor was strengthened every day by removing $^1/_3$ of the old liquor and adding fresh extract and water to raise the barkometer about 2° above that of the preceding day. The pH was adjusted to about 4.5 by the addition of lactic acid for the first week. The duration of tanning was 6 weeks. This process is quite different from the usual countercurrent system in practical operation, in which the astringent liquors are mellowed by contact with almost tanned leather before coming into contact with fresh hides. The high astringency of fresh liquors require that they be used in low concentrations, and penetration of the liquor into the hide is slow. A firm, plump well-filled leather was produced, however, and there is every indication that this extract would be satisfactory, especially if blended and used in a normal tanning process.

Discussion

The successful use of Tennessee Valley oak slabs apparently depends upon the production of two products—wood suitable for pulping, and bark suitable for tanning extract manufacture. The segregation of the bark-wood mixture into only two fractions does not appear feasible. Production of a wood fraction containing only small amounts of bark suitable for pulping necessarily produces a bark fraction with a rather high proportion of wood not suitable for extract manufacture. A bark fraction highly diluted with wood not only raises extraction costs but also has a marked effect upon the quality of the tanning extract. The low purity of the extract from wood is shown in Table

I. Therefore, a high proportion of wood in the extraction mixture causes the production of a low purity extract not suitable for tanning. It is suggested that the bark-wood mixture be segregated into three fractions, the "middlings" to be recycled if feasible and probably discarded in part for other uses, such as fuel.

To improve the economics of extraction and the quality of the tanning extract, it would be desirable to select as far as possible the species of oak to be used. The barks might be classified as follows:

1. Those with high tannin and purity of established tanning value.
2. Those of lower tannin content than group 1 but of good purity, the use of which should be feasible if provided at a low cost.
3. Those of lower tannin content than group 2 but of good purity, the use of which alone would not appear to be feasible but which might be tolerated if mixed in moderate amounts with barks of higher tannin content.
4. Those of low tannin content or purity, the use of which should be kept to a minimum.

According to this classification, the results shown in Table IV indicate that chestnut oak would be the only one in group 1. Southern red, black jack, and black oaks would be placed in group 2; post, scarlet, and white oaks in group 3; and northern red oak in group 4. In classifying the oaks, purity is quite as important as tannin content.

It has been estimated by investigators of the Tennessee Valley Authority [13] that the total cost of preparing extract from 1 ton of airdry slabs would be $8.10. This includes the cost of the slabs and the chipping, screening, segregation, extraction and evaporating costs. The value of the extract produced plus the fuel value of the spent material would be $7.55. If the value of $4.60 for the wood for pulping purposes is added to this, the total value is $12.15. These figures indicate that the process, if used for tanning extract alone, would not be feasible but that it is promising if the wood fraction is profitably utilized.

Data on production and composition of the bark indicate that this potential source of tannin is deserving of consideration. Bailey and Cummings [7] report an annual production of 128,000 cords of air-dry slabs averaging 3,750 pounds per cord and containing 42 per cent bark by weight. On this basis, there should be available annually 100,800 short tons of air-dry oak bark, which, assuming 15 per cent moisture, should be equivalent to 85,680 tons of moisture-free bark. On the basis of a tannin content of 8.6 per cent, which our results have shown, and an estimated extraction efficiency of 80 per cent, this bark should contain 5,895 short tons of 100 per cent tannin. If 80 per cent of the bark is recovered from the chipping and segregating operations, this would indicate as potentially available 4,716 short tons of 100 per cent tannin annually from the oak slabs of the Tennessee Valley area. If all the

slabs were not salvaged and utilized, the potentially available tannin would be less. The amount indicated, however, might be increased if waste from tree tops and branches were salvaged and utilized by the same procedure.

On the basis of the foregoing data, there should be sufficient bark available to operate 2 tanning extract plants, each producing annually more than 15,000,000 pounds of 25 per cent tanning extract or a total of 3,750 tons of 100 per cent tannin. Although this would not represent a major part of our domestic tanning material needs, which recently have averaged about 111,000 tons of 100 per cent tannin annually, it would constitute a worthwhile contribution to our domestic supplies.

Conclusions

Waste oak slabs from Tennessee Valley lumbering operations represent a valuable potential source of tannin. Use of the bark for tannin and the wood for paper pulp are deserving of consideration. If possible, it would be advantageous to conduct the lumbering operations in such a way as to utilize mainly the oak species whose barks are high in tannin.

References

1. Western Hemlock Bark an Important Potential Tanning Material. C. C. Smoot and R. W. Frey. USDA Technical Bulletin No. 566 (1937).
2. Tannin Content of Sitka Spruce Bark. R. W. Frey and I. D. Clarke. *J. Am. Leather Chemists Assoc.* **36,** 576 (1941).
3. Leaching and Tanning Experiments with Tara Pods. J. S. Rogers and C. W. Beebe. *ibid.*, **36,** 525 (1941).
4. Study of the Tannin Contents of Barks from the Florida Scrub Oaks, *Quercus laevis* and *Q. cinerea*. J. S. Rogers, H. N. Calderwood, and C. W. Beebe. *ibid.*, **45,** 733 (1950).
5. Tannin Content and Other Characteristics of Native Sumac in Relation to Its Value as a Commercial Source of Tannin. I. D. Clarke, J. S. Rogers, A. F. Sievers, H. Hopp. USDA Technical Bulletin 986 (1949).
6. Canaigre Investigations I. A Review and Preliminary Report. J. S. Rogers and G. A. Russell. *J. Am. Leather Chemists Assoc.*, **39,** 467 (1944).
   II. Dehydration of Bulk Lots of Canaigre Roots in the Locality Where Harvested. G. A. Russell, J. S. Rogers, and E. C. Stevenson. *ibid*, **39,** 479 (1944).
   III. An Improved Method of Extraction. T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **42,** 118 (1947).
   IV. Fermentation of Liquors for Production of High Purity Extracts. T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **42,** 128 (1947).
   V. Analytical Studies on the Extraction of Canaigre Roots with Water and with Acetone-Water Mixtures. F. P. Luvisi and J. S. Rogers. *ibid*, **43,** 166 (1948).
   VI. Extraction with Organic Solvent-Water Solutions. F. P. Luvisi, T. C. Cordon, C. W. Beebe, and J. S. Rogers. *ibid*, **44,** 707 (1949).
   VII. Fermantation of Extract Liquors and Identity of the Bacteria and Products of Their Growth. T. C. Cordon. *ibid*, **45,** 485 (1950).
   VIII. Preparation of Tanning Extracts by Continuous Countercurrent Extraction. R. M. Rieder, N. F. Roger, G. W. M. Phillips, and R. K. Eskew. *ibid*, **46,** 188 (1951).
   IX. Laboratory Tannage of Heavy Leather. C. W. Beebe, W. S. Kip II, and J. S. Rogers. *ibid*, **46,** 197 (1951).

X. Countercurrent Stationary Vat Leaching of Shredded Canaigre Roots. R. M. Rieder, V. A. Turkot, R. K. Eskew, and G. W. M. Phillips. *ibid*, **46**, 264 (1951).
7. Tannin and Secondary Products from Oak Slabs. L. F. Bailey and W. H. Cummings. *ibid*, **43**, 293 (1948).
8. Tannin from Oak Slabs. E. A. Snow and L. F. Bailey. *ibid*, **44**, 737 (1949).
9. Scrub Oak as a Potential Replacement for Chestnut. H. N. Calderwood and W. D. May. *ibid*, **42**, 62 (1947).
10. Methods of Sampling and Analysis. The American Leather Chemists Association (1946).
11. Natural Tanning Materials of the Southeastern United States. A. Russell. *J. Am. Leather Chemists Assoc.* **39**, 173 (1944).
12. Tanning Materials. Harvey, A. Crosby, Lockwood & Son, London (1921).
13. Oak Slabs and Cordwood as a Source of Tannin and Pulp. E. A. Snow., *J.A.L.C.A.* **47**, 563 (1952).

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Resistance of Sole Leather to Grain Cracking and Piping

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Introduction

An experimental machine has been developed which compacts sole leather by hammering instead of by rolling. This is a through-feed machine which is capable of processing approximately three times as much leather per day as the conventional pendulum-type rolling machine. As the leather passes through the machine, it is subjected to a large number of closely-spaced and overlapping hammer blows which compact it progressively. There are two hammers, spaced several inches apart so that the leather is hammered twice in each pass.

In the development of this machine it was necessary to do a considerable amount of physical testing to make certain that leather compacted on the hammering machine was not inferior in any way to leather compacted by rolling. Two of the physical properties which seemed most likely to be adversely affected by the interrupted action of the hammers were grain cracking and grain piping, and tests were made comparing these properties in the two types of leather.

Test Methods:

The Federal Specifications Board, the Society of Leather Trades Chemists, and the American Leather Chemists Association have methods for making grain cracking tests. The F.S.B. and the A.L.C.A. have a method for making piping tests. All these methods are based on the principle of wrapping a strip of leather around a mandrel of such diameter that the grain is just cracked or piped. In grain cracking the grain is outward and in tension.

In piping it is toward the mandrel and in compression. The cracking and piping tests are made on the same equipment and the same procedures are used.

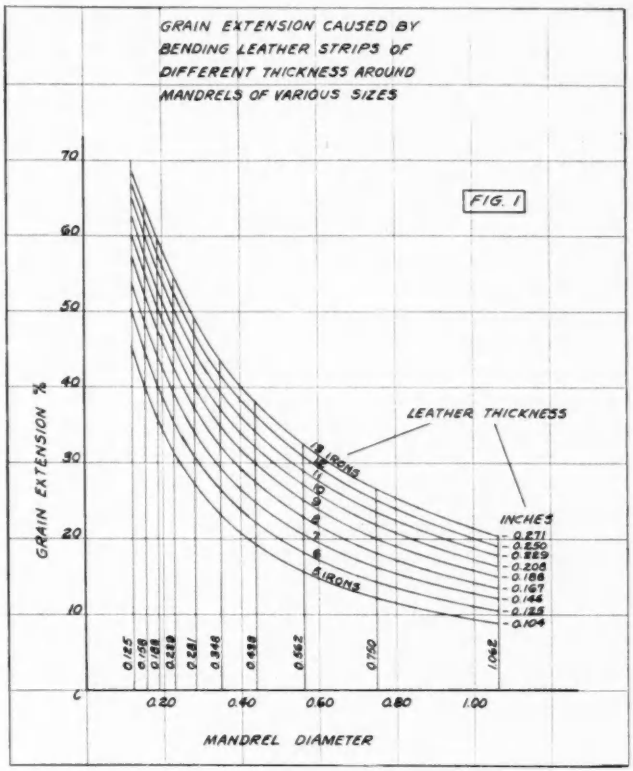
The Federal Specification, KK-L-311[1], has two grain cracking methods, "Cracking, Vise", KK-L-311-4011, and "Cracking, Hand", KK-L-311-4012, and one piping method, "Piping", KK-L-311-4021. These methods were written for specification testing and do not contain some details of procedure and apparatus which are necessary for research and development testing. The Federal Specifications require only that the grain shall not crack or pipe when a specimen is bent around a mandrel of specified diameter. The diameter of the mandrel is part of the specification and is not given in the method.

In research testing it is desirable to determine the smallest mandrel around which a specimen can be bent without the grain cracking or piping. A test method for this type of work should, therefore, list a graduated set of mandrels and the procedures to be followed in bending the specimen around them.

The Physical Testing of Leather Committee of the S.L.T.C. recently recommended the adoption of a "Cracking Test of the Grain of Leather"[2] which contains all the details of mandrel sizes and procedure which are necessary for both research and specification testing. The mandrel diameters, given in centimeters, are so chosen that, if a piece of leather 0.5 cm. thick is bent around successively smaller mandrels, the extension of the grain is increased in increments of 5 per cent. The grain extensions are calculated on the assumption that the neutral axis of bending lies midway between the grain and flesh surfaces. The grain extensions for specimens of any thickness tested on these mandrels can be calculated and used as a measure of the resistance to cracking; a high grain extension indicating a high crack resistance.

If the assumption that the neutral axis of bending lies midway between the surfaces of the specimen is true for cracking, it should also be true for piping. The per cent of grain compression for a specimen of any thickness when bent around a mandrel which just causes the grain to pipe can be calculated and used as a measure of the resistance of the leather to piping; a large per cent of grain compression indicating high resistance to piping.

Because the diameters of the mandrels suggested in the S.L.T.C. method are expressed in centimeters, they do not fit directly into the F.S.B. and A.L.C.A. methods which express all dimensions in inches, irons, and ounces. The diameters of a set of mandrels based on these units were calculated to duplicate as closely as possible those suggested by the S.L.T.C. The mandrel diameters were so chosen that, if a specimen 9 iron thick is bent around successively smaller mandrels, the extension of the grain is increased in increments of 5 per cent. The diameters of these mandrels are given along the abscissa of Fig. 1.



The per cent grain extensions caused by bending specimens of different thickness around these mandrels were calculated and plotted in Fig. 1.

Preliminary Tests:

A set of mandrels with the diameters listed on the abscissa of Fig. 1 and the corresponding bars, as required in the F.S.B. method, KK-L-311-4011 "Cracking, Vise", were prepared.

The device suggested in the S.L.T.C. method "Cracking Test for the Grain of Leather" was built. No drawings of the device were available, but the principles were followed. The mandrel diameters used were those listed on Fig. 1 instead of those suggested in the S.L.T.C. method.

Preliminary tests using 12 iron sole leather were made by each of the methods, KK-L-311-4011 "Cracking, Vise", KK-L-311-4012 "Cracking, Hand", KK-L-311-4021 "Piping" and the S.L.T.C. method. The following observations were made:

1. *Federal Specification Methods.*

The methods, KK-L-311-4012 "Cracking, Hand" and KK-L-311-4021 "Piping", could not be used successfully with heavy, stiff leather because too much effort was required to bend the specimen closely around a full half circumference of the mandrel. Neither a proper cracking nor piping test could be made on a large percentage of the specimens tested.

The principles of the method, KK-L-311-4011 "Cracking, Vise", could be used satisfactorily for both cracking and piping. However, the simultaneous handling of the specimen, mandrel and bar, all loose pieces, and the vise proved to be a task which was practically impossible for a single operator and was cumbersome for two. In this method the mandrel is not firmly supported while the specimen is being bent around it, and it is difficult to pull the leather with sufficient force to wrap it closely around a full half-circumference of the mandrel.

This test can be made more easily by bending the specimen into a "U", placing the bar between the ends and clamping the ends in the vise. The mandrel is then placed in the "U" and pulled against it until the specimen is brought in contact with the mandrel around a full half-circumference.

Performing the test in this manner simplified the handling, but the effort required to bend a heavy specimen to the mandrel was still too great. In those cases where a small mandrel was necessary to crack or pipe the specimen, the mandrel was bent before the specimen could be forced to fit it.

When a specimen does not crack or pipe on the particular mandrel around which it is bent, it is necessary to remove the mandrel, open the vise, remove the specimen and the bar, and retest the specimen on the next smaller mandrel. This procedure is time-consuming and tiring.

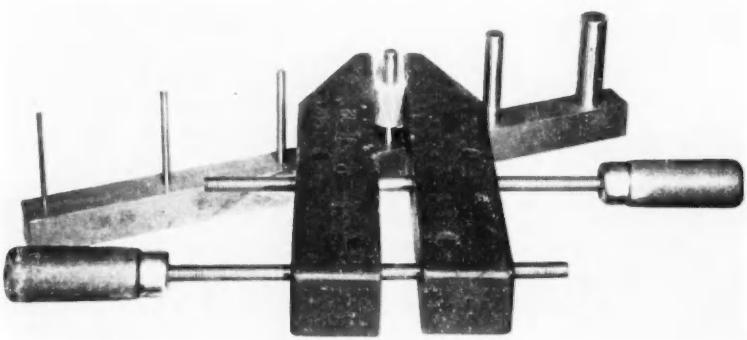


FIGURE 2—Clamp Method.

2. *S.L.T.C. Method.*

This method is excellent in every way except that it is slow to use. Practically no effort is required to wrap the thickest specimen around the smallest mandrel, and a close fit between the two is assured. The only drawback to the method is that, when a specimen fails to crack or pipe on a given mandrel, it is necessary to remove the specimen from the device, change the mandrel adjust the holding pin bar, replace the specimen, and adjust the turning roll. All these changes are time-consuming and make testing by this method rather slow.

3. *Parallel Jaw Clamp Method.*

A modification of the method KK-L-311-4011 was set up as shown in Fig. 2*. In this method mandrels with the diameters shown in Fig. 1 are fastened in a bar which is held in a vise. A specimen is bent into a "U", put between the jaws of a parallel jaw clamp, then placed over a mandrel known to be too large to cause either cracking or piping. The clamp is closed until the specimen is brought into light contact with the mandrel. As the clamp is closed, it is pushed forward lightly so that the specimen stays in contact with the mandrel around the back of the "U". The specimen is lifted in the clamp from the mandrel, placed over and bent to fit successively smaller mandrels until failure occurs. Testing by this method is easier and more rapid than by the method, "Cracking, Vise", and faster but not easier than by the S.L.T.C. method.

CRACKING TESTS:

Test No. 1

A test was designed to:

1. Compare the results obtained by:
   a. The F.S.B. method, "Cracking, Vise".
   b. The S.L.T.C. method, "Cracking Test for the Grain of Leather".
   c. The Parallel Jaw Clamp method.
2. Determine the effect of specimen thickness on the cracking of the grain.
3. Compare the crack resistance of the grain of rolled and hammered stock.

Specimens.

Three heavy bends of sole leather which were compacted by rolling and three bends made in the same lot and treated the same in every respect, except that they were compacted by hammering, were cut into strips, $^1/_2$ inch by 6 inches. The long axes of the strips were parallel to the backbone. There were 144 strips cut from each bend.

*The bar shown in Fig. 2 was used in preliminary tests only and has only the alternate mandrels from the set used in later work.

The strips from one bend were thrown in a pile and mixed, then divided at random into 4 groups of 36 pieces. A group of 36 strips was taken from each of the three bends compacted by rolling and combined into a single group of 108 specimens. The specimens in the four groups, thus formed, were split to 11, 9, 7 and 5 irons. The specimens from the hammered bends were combined in the same manner and split to the same thickness as the rolled specimens.

Method of Test:

A specimen was tested at the center by the Clamp method and the mandrel size required to cause grain cracking was determined. One end of the specimen was then tested by the "Vise Cracking" method using a mandrel of the same diameter and whether or not the grain cracked was noted. Those specimens which did not crack were not tested on smaller mandrels. The other end of the specimen was tested by the S.L.T.C. method. The specimen was bent first around the mandrel next larger than that found to produce cracking by the Clamp method and then around successively smaller mandrels until the grain cracked.

Results:

The diameters of the mandrels about which the grain of the 108 specimens in each group cracked in the Clamp method and in the S.L.T.C. method were averaged. These averages are given in Table I, Columns II, IV, V and VII. Columns III and VI give the number of specimens out of a group of 108 which cracked on the same sized mandrel when tested by the "Vise Cracking" and the Clamp methods. Column VIII gives the overall average of the mandrel diameters on which all specimens of a given thickness cracked. Tests by the S.L.T.C. and the Clamp methods on both types of leather, totalling 432 pieces of data, were averaged to obtain each value in this column. The grain extensions based on the average mandrel diameter and the leather thickness were calculated to obtain the values given in Column IX.

TABLE I

	Rolled Leather			Hammered Leather			Overall	
	Ave. Mandrel Diameter			Ave. Mandrel Diameter				
Thickness	Clamp	Vise No.	S.L.T.C.	Clamp	Vise No.	S.L.T.C.	Diamter Ave.	Strength of grain
11 iron	.56	100	.54	.55	98	.52	.54	29.9%
9 "	.46	96	.45	.42	97	.43	.44	20.9%
7 "	.37	102	.37	.31	98	.31	.34	30.0%
5 "	.25	99	.24	.23	92	.24	.24	30.2%

CONCLUSIONS:

1. There is no significant difference in the results obtained by using the three test methods.

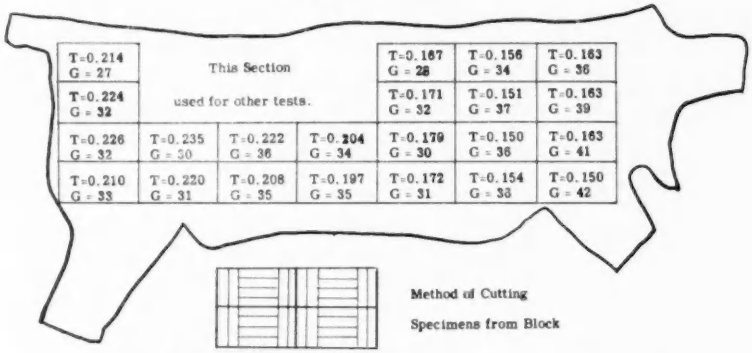
2. The neutral axis of bending lies either midway between the two surfaces of the specimen or at some other constant proportional distance between them. The position of the neutral axis is unaffected by the thickness of the specimen, and it does not change as the leather is split and the grain layer becomes an increasingly larger part of the specimen.
3. The data shows that the average mandrel diameter about which the hammered leather cracked is consistently smaller than that about which rolled leather cracked. Analysis of the data showed that while hammered leather may not be significantly more crack resistant than rolled leather it is certainly not less resistant. It is safe to conclude that the interrupted action of hammering does not adversely affect this property.

Test No. 2

This test was designed to:

1. Compare the crack resistance of rolled and hammered leather at various locations in the skin.
2. Compare the resistance of hammered leather to cracking when bent along and across the direction of the hammer axis.

Effect of Location on Crackiness.



T = Average Thickness
G = Average Grain Extension
Averages based on 48 specimens
8 specimens from each block-both directions averaged.
6 blocks - 1 from same location in each side.
both types of Compacting Averaged.

Fig. 3

Specimens:

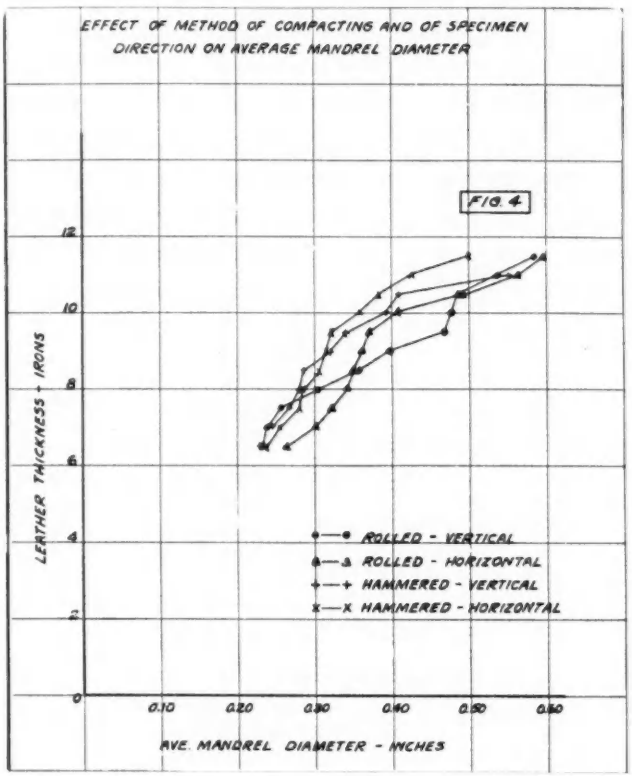
Three sole leather sides which had been compacted by rolling and three sides from the same lot compacted by hammering were cut into rectangular blocks, 8 inches by 4 inches, as shown in Fig. 3. Specimens for other tests were cut from the section so marked. Each block was cut into 8 specimens, 1 inch by 4 inches, so that the axes of 4 specimens were parallel to the backbone, and the axes of the other 4 were perpendicular to the backbone.

Each specimen was numbered so that the method of compacting, its location in the hide, and the direction of its long axis was known. The thickness of each specimen was measured to the nearest $^1/_2$ iron at the center.

A skin is fed into the hammering machine so that the axis of the hammer is across the side or perpendicular to the backbone. A specimen is tested with its long axis around the mandrel and it cracks across its axis. From these facts, it follows that a specimen cut with its long axis parallel to the backbone of a hammered side will crack in a direction parallel to the axis of the hammer.

Method of Test:

The Clamp method, described above, was used for these tests.



Results:

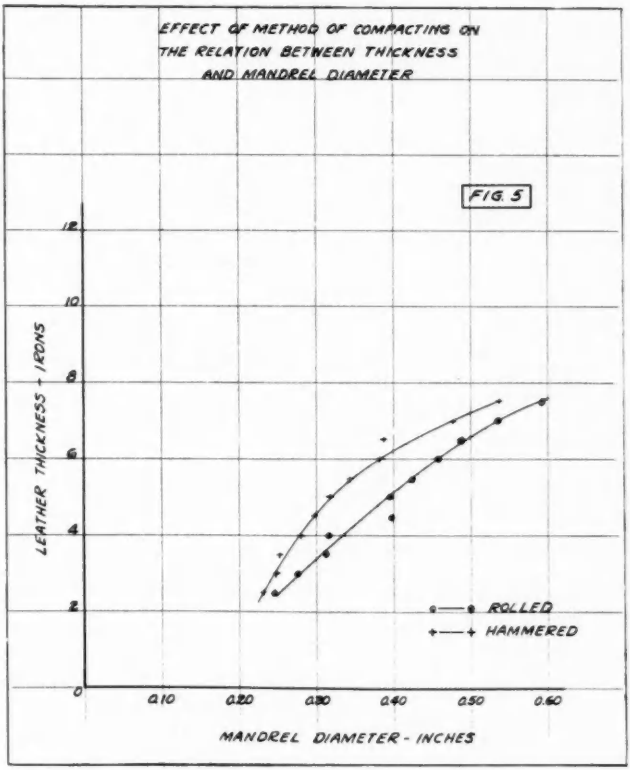
1. *Effect of Direction*

The data were separated into groups so that the specimens in a group

were all of one thickness, compacted by one method and cut with their long axes in one direction.

The diameters of the mandrels on which the grain of the specimens in each group cracked were averaged. The results are plotted in Fig. 4. Between 20 and 50 values were averaged to obtain each point on the plot. Lines are drawn between the individual points to aid in separating the data and not with any thought that the lines indicate the trend of the individual curves. The curves representing the four conditions of the test show that the data overlap to some extent, but an analysis of the data shows that:

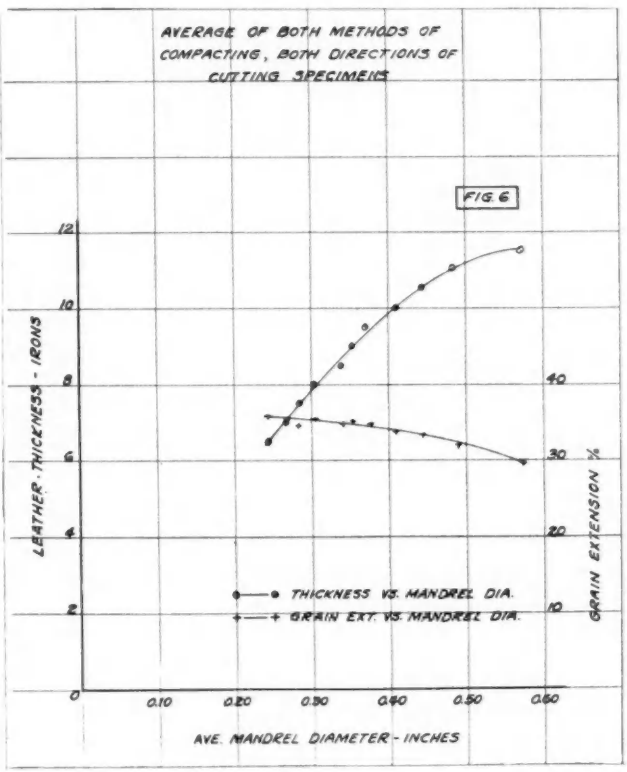
a. The direction from which the pecimen is cut from the skin and hence the relation of the direction o ·racking to the direction of compacting has no significant effect on ıe resistance to grain cracking of either rolled or hammered leather.



b. Hammered leather has a small but significantly greater resistance to grain cracking than rolled leather.

2. *Effect of Method of Compacting*

If the direction from which the specimen is cut has no influence on its resistance to grain cracking, the diameters of the mandrels required to crack all the specimens of a given thickness and method of compacting can be averaged without distorting the results. These averages were calculated and are plotted in Fig. 5. The curves show clearly that the average diameter of the mandrel required to crack the grain on hammered leather is less than that required to crack the grain on rolled leather of the same thickness and, therefore, the grain of hammered leather has greater average extension at failure and is slightly more resistant to cracking than the grain on rolled leather.



3. *Effect of Thickness*

If neither the direction of the specimen nor the method of compacting have more than slight influence on the resistance of leather to cracking, the diameters of the mandrels required to cause all specimens of a given thickness to fail can be averaged without distorting the results. These averages were calculated and are plotted in Fig. 6. The average diameter of the mandrels required to crack all specimens of a given thickness was used in calculating the average grain extension for the specimens of each thickness. These values are also plotted in Fig. 6.

The curves show that in unsplit leather the resistance to cracking, i. e., the extension of the grain at cracking, decreases as the thickness of the leather increases. This does not agree with data for split leather (Test No. 1) in which a constant grain extension at cracking was found. When, as in these tests, practically a whole side is cut into specimens, thick specimens tend to come from definite skin location and thin specimens from other locations. It is possible, therefore, that the variations due to thickness which are shown in this test are, in reality, variations due to the location of the specimen in the skin.

4. *Effect of Location*

The data for the 8 specimens in the blocks taken from a similar location in each of the three hammered sides and the three rolled sides were separated into groups. Each group contained the data from 48 specimens, 8 specimens from each of 6 blocks. No separation, because of the direction in which the specimen was cut nor because of the method of compacting, was made. The average thickness of the specimens and the average diameter of the mandrels on which the grain of the 48 specimens in a group cracked were determined. These values were used to calculate the average grain extensions at cracking.

The average specimen thickness and the average grain extension for each location are shown in Fig. 3.

The data show that the leather near the backbone in the rump and bend has lower crack resistance than that from any other part of the skin and that the crack resistance is greater in the leather along the lower edge of the side.

Test No. 3.

COMPARISON OF LEATHER FROM VARIOUS TANNERIES

Specimens:

The leather used in Test No. 1 was made by Tannery A; that used in Test No. 2 was made by Tannery B. Three rolled and three hammered bends were secured from Tannery C and cut into 1 inch by 4 inch specimens. The long axis of all specimens was parallel to the backbone. The thickness of the specimens was measured to the nearest $^1/_2$ iron.

TABLE II

Thickness of Specimens (Irons)	TANNERY A				TANNERY B				TANNERY C			
	Number of Specimens	Grain Extension Per Cent			Number of Specimens	Grain Extension Per Cent			Number of Specimens	Grain Extension Per Cent		
		Max.	Min.	Ave.		Max.	Min.	Ave.		Max.	Min.	Ave.
5.0	432	35.5	23.0	29.9								
6.0					16	50.0	35.5	37.2				
6.5					52	51.5	28.3	35.7				
7.0	432	39.0	25.0	29.9	126	53.8	29.6	35.5				
7.5					133	55.1	31.2	35.4				
8.0					133	47.5	27.5	35.2	12	54.3	39.0	46.3
8.5					94	48.7	24.0	34.7	14	54.0	39.1	45.8
9.0	432	39.5	25.0	30.0	103	50.0	25.0	34.5	40	52.7	36.0	45.1
9.5					81	51.2	26.0	34.6	27	51.8	34.6	44.1
10.0					127	52.5	21.5	33.7	80	50.8	35.6	42.7
10.5					98	49.0	22.5	33.2	63	50.0	33.5	41.0
11.0	432	39.5	23.5	30.2	102	44.5	23.4	32.0	58	48.3	30.3	39.2
11.5					45	46.0	24.3	29.3	38	46.0	26.4	38.1
12.0									19	42.5	26.1	36.5
12.5									14	37.0	23.8	34.2
13.0									2	26.5	20.0	24.1

Method of Test:

The specimens were tested by the Clamp method.

Results:

The data were separated in groups according to the tannery from which the leather was secured and the thinckness of the specimen. The average of the diameters required to crack the grain on the specimens of a single group was determined.

Using the maximum, minimum and average diameters of the mandrel on which the specimens of a given group cracked, minimum, maximum and average grain extensions for the specimens in the group were calculated. These values for the leather from the three tanneries are tabulated in Table II.

The data show a wide difference between the maximum and minimum values of the grain extension at cracking for the leather from each of the tanneries. This indicates that crack resistance, like most other physical properties of leather, has a high degree of variability. The results also show a large difference in the average resistance to grain cracking in the leather from the different tanneries.

Piping Tests:

Attemps to make piping tests on rolled and hammered leather taken from the same tannery lot failed completely because neither type of leather could be made to pipe even when bent around a mandrel which was so small that the flesh side of the leather tore in the process.

The condition of the grain layer was observed by several people with leather experience who all agreed that while distortion of the grain occurred it was not the type of distortion usually considered to be piping.

The grain on pieces of leather cut from insoles 4 to 7 irons thick which were found in the laboratory could be piped on mandrels ranging in diameter from 0.229 inch to 1.0625 inch. While only a very few tests were made, it appeared that the Clamp method was satisfactory for the test.

References

1. Proposed Revision of Federal Specification, KK-L-311, May 1, 1950.
2. Report of the Physical Testing of Leather Committee, *J.S.L.T.C.*, **36**, 206 (1952).

Received Nov. 8, 1952.

BOOK NOTICE

Chemical Engineering Operations. By F. Rumford. Cloth, 376 pages. Chemical Publishing Co. Inc., 212 Fifth Ave., New York, N. Y. The presentation of chemical engineering in this book is confined to seventeen of the most common operations peculiar to the chemical industry. It does not attempt to completely cover the engineering field, leaving out power generation and transmission, rheology and other general subjects except as they apply directly to the equipment or operation described. There is a short but excellent chapter on

heat transfer. For the student it is obviously supplemental to the foundation study. It is the sort of book which is needed in taking the step from abstract theory to practical operation. As such it is also valuable to the plant engineer, particularly for the development of new processes. It takes the reader down to the fundamental principles, clearly expressed, and then shows their practical application with plentiful illustrations. It makes a good compact guide for plant design of engineering processes. R. H. T.

Wax Chemistry and Technology. By L. Ivanovsky. Paper pamphlet. 44 pages. Published by Soap, Perfume and Cosmetics, 24 Bride Lane, Fleet Street, London E.C. 4. This little monograph does an excellent job of reducing the jumble of wax nomenclature and properties to some semblance of order. To the nonspecialist in the field, who is nevertheless obliged to purchase and use waxes, it should prove most valuable. The author points out that there was relatively little commerce in waxes up to the beginning of the present century. Yet the uses of waxes are age old. The effort of the merchandizers to capitalize on the old names has led to a situation where names are often entirely misleading. In the classification waxes are divided into five main groups: hydrocarbon waxes, pseudoester waxes, acid waxes, alcohol, ketone and ether waxes and ester waxes. These are subdivided into sixteen sub-groups made up of forty-two representative types. There is a brief description of each type and references for those who wish to go into the subject further. R. H. T.

ABSTRACTS

Study of the Variation of the Physical and Chemical Properties of Chrome-Tanned Leather and the Selection of a Sampling Location. By J. R. Kanagy, C. W. Mann and John Mandel. *J. Soc. Leather Trades' Chemists*, **36**, 231 (1952). A study was made of the variation of the physical and chemical properties of split chrome-tanned leather over the area of the side, of unsplit chrome-tanned leathers similar to the split and chrome-retanned cow and steer hides. The split and unsplit leathers were chrome-tanned and stuffed steer hides. Hides were cut into two sides, one of which was split for making upper

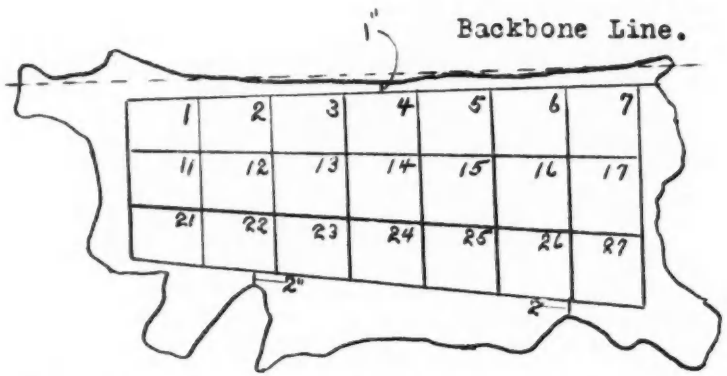


FIGURE 1.—Relation of sampling area to the side and the design used in cutting the sides into blocks.

leather, the other remained unsplit. Both were subjected to identical tanning and finishing. This made possible a study of the correlation between sides of the same hide where the only difference was the splitting of the side. The sides were divided into 21 blocks as shown in Fig. I. A plan is given for cutting the specimens from the 21 blocks. In each there are four locations for tensile strength, one for density, one for burst, vapor permeability and resistance to water penetration. Analyses were made for chromic oxide, ash, hide substance and grease. In all strength tests, in which directional effect might be expected, specimens were cut parallel and perpendicular to the backbone. Physical and chemical test methods used are as described in U. S. Federal Specifications KK-L-331 except that water penetration was measured by the dynamic method developed by Maeser. The strength tests and burst tests were made in a 2000 pound capacity Tinius Olsen machine. Water permeability was measured by the method developed by Kanagy and Vickers. Correlation of the averages of tests for a side and each block were made. Correlation studies were also made between the various physical test methods on a side to side and block to block basis. Only blocks 4, 5, 6, 7, 14, 15, 16 and 17 had any appreciable amount of hide removed by splitting. Where sides are split appreciably the unsplit leather is stronger than the split. Bursting strength, tongue tearing and stitch tearing are higher in the middle row and belly areas than in the butt and backbone area. In general tensile strength averages 20 per cent greater in the parallel than in the perpendicular direction. Blocks 7, 21 and 26 are exceptions. Stitch-tear shows even greater strength in the parallel direction. Tongue-tear varies little with direction. Average bursting strength, on thickness basis, is greater for split leather. Correlation, using block averages, is higher in every case than when using side averages, illustrating the importance of sampling corresponding locations between hides in research studies. Blocks 5, 15 and 25 give the lowest average percentage coefficients of variation; and the blocks located in the butt and shoulder areas at opposite ends give the highest. In a supplementary experiment on ten chrome-tanned steer hides the average breaking loads are higher in the parallel direction in all cases. The breaking load of the splits in either direction appears to be a straight line function of thickness. The splits show uniform stitch-tear strength, based on unit of thickness down to about 55 mils, at which point a sharp drop takes place. Chemical analyses show that moisture and chrome content vary with the hide substance, the ratio of moisture to hide substance being about 0.2 and the ratio of Cr_2O_3 to hide substance approximately 0.65. Grease and hide substance vary in the opposite direction, resulting in a variation as high as 100 per cent between blocks 21 and 7, the former being about double the latter. The Cr_2O_3 is multiplied by the Kubelka factor, 2.73, to convert to chrome tanning substance. The sum of hide substance, grease, $Cr_2O_3 \times 2.73$ and ash minus Cr_2O_3 gives totals varying between 97.6 and 101.5 per cent of the leather used. The principal criterion for the selection of sampling location is the correlation coefficient between results obtained for a test in a specific position and the average result for that particular test for the entire side. For tensile strength blocks 5, 6, 12, 13, 15 and 16 are best; for bursting strength blocks 14, 15 and 17; for stitch-tear 1, with 2, 6, 7, 11 and 12 second. Averaging all factors the best blocks, if only one block is to be taken, are 12 and 7. The latter is chosen because it can be located accurately and is on the edge of the hide. Since there is little variation in chemical analyses due to position, the waste from the test pieces cut from block 7 may be used for that purpose. R. H. T.

The Influence of Size of the Tannin Molecules on Vegetable Tannage. By R. O. Page. *J. Soc. Leather Trades' Chemists*, **36**, 253 (1952). Previous work has indicated that in wattle extract solutions the number of dark large sized molecules can be increased by exposure to light and air or by long heating. In this study hide powder was tanned with wattle extract solutions in which the number of larger molecules was varied either by these

means or by changing the ratio of hide powder to tannin. Tanning took place in closed containers excluding light and air unless the action of these was being studied. In the latter case the tannin solution and air were alternately circulated through the hide powder. Hide powder tanned for one month with and without exposure to air gave the following results in which the first figure is without and the second with light and air. Combined water solubles 38 and 24. Degree of tanning 58 and 92. Total combined tannin 96 and 116. The greater combined tannin is probably due to increase in size of the tannin molecules but could be caused by precipitation in the hide powder of insolubles formed by action of light and air on the tannin. To test which might be true tanning was done with wattle extract exposed to light and mixed with air for three weeks and also with extract in which the molecular size had been increased by heating. The latter gave a 63 degree of tannage as against 52 for the former and combined tannin of 115 as against 111 for the former, indicating that the increase in combined tannins is due to the increase in molecular size. In another test a three months tanning was done with excess wattle extract never changed and with similar extract changed frequently. There was considerably greater combined tannin with the changed liquor, indicating a selection of preferred tannin molecules. Hide powder, tanned for varying periods up to 48 months in unchanged liquor not exposed to light and air, came to practical equilibrium for the total combined tannin in 9 months. This apparent equilibrium is attained in 3 months with change of tan liquor and in one month with liquors treated to increase size of tannin molecules. In practice there is a rapid initial tanning up to a degree of tannage of about 50. At ordinary temperature tannage thereafter is very slow and does not result in an increase in shrink temperature. The author explains this by assuming that small molecules rapidly penetrate and satisfy all tannage bonds, but are later displaced by slowly penetrating large molecules which increase the degree of tannage but do not increase shrink temperature because no new bonds are made. R. H. T.

The Influence of Acids and Salts in Sole Leather Tannage. Part II. By H. Anderson and L. Daniel. *J. Soc. Leather Trades' Chemists*, **36**, 259 (1952). In part I a quantitative relationship was established between the degree of hydration and the amount of tannin fixed by fibers. Although amount of swelling depends upon the properties of the pelt, temperature, type and quantity of acid and salt, and the pH, hydration was effectively controlled by additions of salt wherever acid swelling was present. When pelt pieces were tanned in a liquor which had the same pH, acid and salt content as the swelling medium, tannin fixation was found to change with salt concentration in such a way that the ratio of fixed tan yield to hydrated weight was constant and independent of the pH and salt concentration. In a further study, comparing two sets of pelt pieces, one set was tanned in 40 degree Bk. mimosa, the other was brought to osmotic equilibrium with salt and acid solutions equivalent to the tan liquors in which they were to be tanned. Both sets were tanned 34 days. Variable amounts of sodium sulfate were added in both cases. In the equilibrium set the degree of tannage decreased with increase in salt and fixed tan weight to hydrated tan weight times 100 was constant at 47. In the other set the lowest salt concentration gave the highest degree of tannage; but there was not relationship between the amount of salt added and the degree of tannage. Only where acid swelling is present can the repressive action of salt on pelt plumping oe observed. Practical tannage can be regarded as the tanning of double laminae under conditions of increasing plumping force and tan penetration rate, the exact values of these depending on each individual tannage. Plumping force is best controlled by regulation of pH and salt content. R. H. T.

Combination Tanning Process for Making Heavy and Light Leather. By R. Bosse. *Das Leder* **3**, 97 (1952). Chrome pretannage with cationic complexes results in increased

fixation of vegetable tannin by increasing the reactivity of the skin and also by the creation of new combining possibilities with the chrome complex. In a comparison of normal hide powder and powder pretanned with 33 per cent basic chromium sulfate (2.75 per cent Cr_2O_3 on the dry hide powder basis), pretanning increased the tan value by 11 per cent and the combining value by 30 per cent. A greater degree of prechroming did not change the tan value but increased the combining value by up to 45 per cent. Syntans also increase combining value. The value of chrome pretanning for heavy leather is well known. One can bring prechromed hides into concentrated liquors without case hardening and with a greatly shortened time of tannage. Leathers can be obtained with various properties intermediate between those of chrome and vegetable leathers. High quality vegetable sole leather was formerly made at Leverkusen by the following method. The hides were limed as usual then delimed thoroughly with ammonium sulfate or sodium bisulfite. Rapid deliming could also be obtained with 2.5 per cent Oropon VS and 0.25 per cent hydrochloric acid. The hides were pickled with 150 per cent water, 12 per cent salt and 3 per cent hydrochloric acid. Thorough pickling was important for uniform chrome distribution. The hides were lightly chrome tanned in about 5 hours in a bath containing 150 per cent water, 0.6 per cent chromium oxide and 3 per cent salt. Plumping can be regulated by varying the proportion of salt. After neutralization with 0.3 per cent soda (1:20 solution) the pH of the float was 4.7-5. The leather was then left on a horse for 2 days. The hides were rinsed, drummed a couple of hours in 200 per cent water and 2 per cent sodium bicarbonate at 35°C, then another hour after addition of 4 per cent of a neutral syntan such as Baykanol G. The hides could be put into strong liquors but it was preferable on account of necks, to first put the hides for 1 day each in liquors of 2°, 4° and 6° Bé. They were then tanned in from 4 to 6 days in a liquor starting at 10° Bé and strengthened to 16° Bé. In choosing the vegetable tannin, one should remember that prechroming gives a softer leather than is obtained without chroming. Retanning of upper, clothing and white leathers are also described. I.D.C.

Retanning Chrome Leather with Vegetable Tanning Materials. By G. H. W. Humphreys. *Das Leder* **3,** 145 (1952). The vegetable tannin for retanning should have good astringency, suitable particle size so penetration will not be too great, and a pH value such that it will neutralize residual acidity from the chrome tanning. Neutralization before retannage is required if the leather must have high strength but neutralization aids penetration of the vegetable tannin. If a tight grain is desired and strength is less important, neutralization may be omitted. Fatliquoring is usually done after retannage in England, but on the continent it often precedes retanning, however the former is preferable. I.D.C.

Gambier Nontanins and the Special Effect of Aromatic Complexformers on Chrome Leather. By Gerhard Otto. *Das Leder* **3,** 121 (1952). Retannage of mineral tanned leather with gambier produces leather with a smooth, tight grain. Gambier also promotes level dyeing of chrome leather. Titration curves of gambier extract and gambier non-tannin resp., below pH 4.5, showed that the titrating acid was reacting with salts of weak acids of the nontannin. By electrophoresis 23 parts of anionic material was separated from 100 parts of dry substance. Analysis showed that one-fourth of the anionic fraction was aromatic and that the molecular weight of both the aromatic and the aliphatic material was about 150. The latter was dicarboxylic. The aromatic acid might be 2,4-dihydroxybenzoic and the other, adipic acid. Dihydroxybenzoic acid was found to be twice as effective as gambier nontannin in reducing the shade of chrome leather black E extra on retanned chrome leather, and also in increasing penetration of mimosa in chrome leather. Aromatic anions have complexforming tendencies intermediate between those of various nonaromatic anions, but they surpass other anions in their effect on the above mentioned dye and on pene-

tration of mimosa. For example, when used to pretreat chrome leather before retanning with mimosa the order of increasing effect on penetration of the tannin was as follows: $SO_4^{=}$, CNS^{-}, CH_3COO^{-}, $HCOO^{-}$, succinate, $SO_3^{=}$, tartrate, lactate, glycollate, maleinate, malonate, *phthalate*, oxalate, citrate OH^{-}, *sulfophthalate*, *sulfosalicylate*, *dihydroxybenzoate*. On the basis of this work patents have been obtained on products that can be used in place of the more expensive gambier. The advantages of certain complexforming aromatic anions were as follows: In the pickle, sulfosalicylic, sulfoanthranilic, or sulfophthalic acids produced fullness and fine grain. In the chrome tanning process, sulfophthalic or dihydroxybenzoic acids produced fullness and improved flanks. Phthalate in tanning or neutralization produced fullness and uniformity of dyeing. Sulfosalicylate or sulfoanthranilate caused a mild, uniform vegetable retannage. Sulfophthalate gave a fine, firm grain and dihydroxybenzoate an elastic grain if used before vegetable retannage. I. D. C.

A New Practical Method for Testing Fish Oil Regarding Its "Tanning Value" in Chamois Tanning. By J. A. Sagoschen and V. G. Czepelak. *Oesterreichische Leder-Zeitung* **7,** 89 (1952). A practical oil tanning test is made by the following method: Cattle hide grain splits (1.5 mm. thick when dry) are used after they have been limed, delimed, bated then dried. Pieces, 12 x 18 cm., are soaked in water at 20° for 48 hours then at 30°C for 30 minutes, working the skins thoroughly by hand. The skin is then dehydrated by two, three-hour treatments in 96 per cent alcohol then one hour in ether. Direct from the ether the skin is oiled, wrung, reoiled and wrung, then oiled and hung in the air at 25°C for one hour to oxidize. After working more oil into the leather it is left overnight at 25°C or at 30C° if the oil has a higher melting point. Oiling and oxidizing is repeated until tannage is complete. This normally requires 4 or 5 days, although the best oils require only 3 days and some oils 9 days. Thoroughness of tanning is tested by washing a clipping in soda solution at 35°, drying, extracting with ether then examining for softness and appearance. After tanning, the leather is washed in a large volume of 0.2 per cent soda solution at 30°C then thoroughly in water at 35°C. If fat is to be determined later by extraction with ether, the leather should be dipped in 1 per cent acetic acid to liberate fatty acids from soaps before the leather is airdried. For comparison, a standard sample of cod oil, having an acid number of 35-40 and an iodine number of 140-150, should be used. I. D. C.

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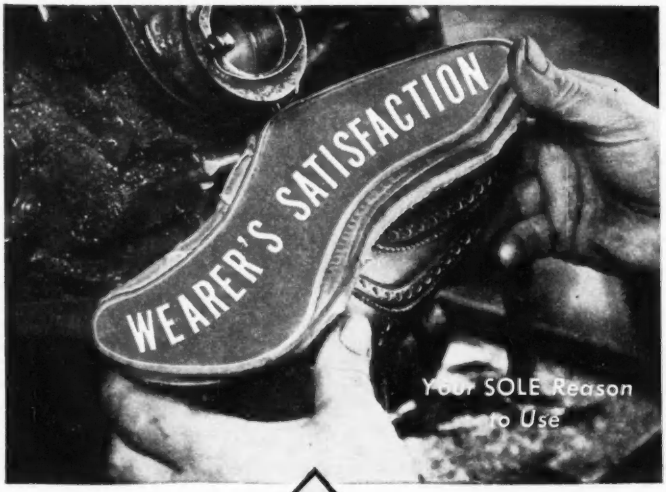

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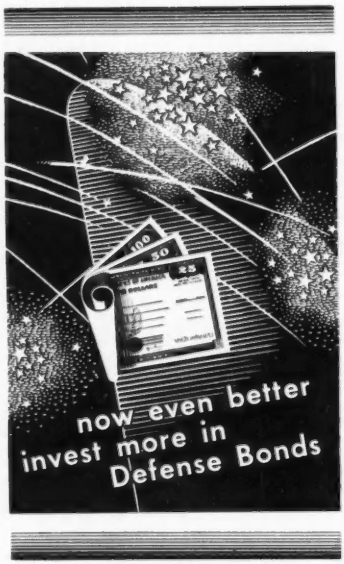

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549 W. Washington Blvd. Chicago, Illinois

MYRTAN

A TANNING EXTRACT

made from the wood of an Australian species of the Eucalyptus family. It contains both catechol and pyrogallol tannin, the latter predominating.

TYPICAL A.L.C.A. ANALYSIS

TANNIN	61.55
NON-TANNIN	16.03
INSOLUBLES	1.70
WATER	20.72

Also Available as Liquid with 30% Tannin

As a retanning agent for chrome tanned leather, Myrtan possesses many advantages, such as smooth and strong grain, good color and break, as well as a round feel.

Blended into sole leather tannages, it has given better yields and improved color.

For further information address:

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